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NATIONAL INSTITUTE OF STANDARDS &  
TECHNOLOGY  
Research Information Center  
Gaithersburg, MD 20899





National  
Measurement  
Laboratory

**Center for  
Materials  
Science**

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**Annual  
Report  
1982**

NAS-NRC  
Evaluation  
Panel

November 18-19, 1982



U.S. Department of  
Commerce  
National Bureau of  
Standards

**NBSIR 82-2609**

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## Annual Report 1982

NAS-NRC  
Evaluation  
Panel

November 18-19, 1982

John D. Hoffman, Director  
National Measurement Laboratory

Robert Mehrabian, Director  
Center for Materials Science

**NBSIR 82-2609**





## ABSTRACT

The Center for Materials Science is part of the National Measurement Laboratory, one of the three major units of the National Bureau of Standards. Research programs in the Center's five technical divisions cover the major classes of materials (metals, polymers, ceramics, glass and composites) and address basic needs for materials measurements, standards, and data. The Center provides generic technical support for optimum efficiency in processing, fabrication, and utilization of materials. Program output is disseminated to a wide range of industrial users and university researchers by means of workshops, industrial guest worker interactions, formal and informal laboratory and planning visits, Center staff standards committee activities, technical publications, and seminar programs. Two key outputs are standard reference materials for measurement calibration and evaluated standard reference data. The Center undertakes materials research in NBS mission areas to support measurements and standards needs of other Federal agencies. This volume summarizes the technical activities and accomplishments of the Center for Materials Science for FY82.



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## INTRODUCTION

The Center for Materials Science (CMS) is located within the National Measurement Laboratory (NML), one of the three principal laboratories comprising NBS. The organization structure of the CMS, NML, and NBS, is given in the Appendix. The Center for Materials Science, one of the largest Centers at NBS, has approximately 310 staff members (and approximately 120 guest workers and research associates); ~ 83 percent of the staff are professionals; of these 55 percent hold Ph.D. degrees. The operating budget of the Center for FY82 amounted to ~ \$23 M.

The Center for Materials Science is responsible for providing data, measurement methods, standards and reference materials, concepts, and technical information on the fundamental aspects of processing, structure, properties and performance of materials to industry, government agencies, universities, and other scientific organizations. The programs of the Center support wide generic technologies in materials in order to foster their safe, efficient, and economical utilization to meet our national needs within the framework of the materials cycle. The Center also makes a significant contribution as a national resource of materials information through its four Data Centers.

The long-term goal of the Center for Materials Science is to support the private sector and other Government agencies in the most effective application and utilization of materials--metals, polymers, and inorganic materials. Center activities in FY82 focused on those aspects of materials research involving processing science, structure/property science, and durability science. More specifically the Center:

- Develops and maintains scientific competences and experimental facilities to provide the Nation with a central basis for uniform physical measurements, measurement methodology, and measurement services necessary to defining the properties and performance of materials and to other essential areas in the materials science discipline.

- Provides technical information in the form of reference data, materials measurement methods, and standard reference materials. Information is provided to other agencies of Government, universities, consumers, and to industrial processors, designers, and materials users to enable them to select cost effective combinations of materials, processes, designs, and service conditions.

- Through its measurement research programs, characterizes the structures of materials, chemical, mechanical, and physical properties which have wide application throughout the technical community as a basis for the safe, efficient uses of materials, the improvement of materials technologies, and the development and design of innovative materials.

- Obtains and disseminates accurate experimental data on the behavior and properties of materials over time under service conditions to assure effective utilization of manufactured materials.

The Center is organized in five Divisions, having responsibilities in different areas of materials science. The research activities of the Divisions are structured according to a task system; each task has specific goals, objectives, and milestones which support the overall goals of the Center. The following listing tabulates the tasks for each Division. Detailed descriptions of the FY82 technical activities encompassed by the various tasks are given in the following sections.

## Task Numbers, Titles, and Leaders

### 560 Center Office

12101	Microstructure of Materials	J. B. Wachtman, Jr. to 8/22/82 R. Mehrabian from 8/22/82
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### 561 Materials Chemistry Division

12113	Corrosion and Protection of Metals	J. Kruger
12114	Materials Biotransformations and Chemical Durability in Service Environments	F. E. Brinckman
12115	High Temperature Materials Chemistry for Processing and Durability	J. W. Hastie
12154	Properties, Structure, and Standards for Glass and Optical Materials	W. K. Haller
12156	Ceramic Processing and Durability Science	T. Negas
-----	Recycled Oil Program	S. Hsu

### 562 Fracture and Deformation Division

12121	Fracture Mechanisms and Analyses	E. R. Fuller, Jr.
12122	Durability of Ceramics and Composites	S. M. Wiederhorn
12123	Elastic Plastic Fracture Mechanisms	H. I. McHenry

### 563 Polymer Science and Standards Division

12132	Polymer Standards for Process Control and Equity	I. C. Sanchez
12135	Tests, Standards, and Characterization for Manufacturing and Durability of Dental and Medical Materials	J. M. Cassel
12136	Mechanical Durability of Polymers	B. M. Fanconi
12137	Processing and Reliability of Polymer Composites	B. M. Fanconi
12138	Additive Migration and Chemical Durability of Polymers	F. W. Wang
12139	Dielectric Plastics: Microstructure and Performance	G. T. Davis

### 564 Metallurgy Division

12142	Structure Characterization	M. Kuriyama
12143	Metallurgical Processing	J. R. Manning
12144	Mechanical Properties and Wear	A. W. Ruff
12145	Chemical Metallurgy	R. Mehrabian
51105	Synchrotron Radiation Research for Materials Science	M. Kuriyama

566 Reactor Radiation Division

12161	Reactor Operations and Services	T. M. Raby
12162	Neutron Scattering Characterization of Materials for Advanced Technologies	J. J. Rush
12163	Neutron Structure Methods and Crystal Data Base for Materials Utilization	J. J. Rush
51102	Advanced Neutron Methods	J. M. Rowe



## OFFICE OF THE CENTER FOR MATERIALS SCIENCE

John B. Wachtman, Jr., Director to 8/22/82  
Robert Mehrabian, Director from 8/22/82  
Darrell H. Reneker, Deputy Director  
Suzanne H. Bussard, Secretary

The Center Office is responsible for providing the technical and administrative framework for the planning and operation of the programs carried out by the five technical Divisions and the Center Office scientists.

The Center provides technical support to the Administration's activities on national materials policy. A draft chapter on Technical Trends in Materials use was prepared for the Office of Strategic Resources, Department of Commerce study of Critical Materials Requirements of the U.S. Steel Industry. This study is a response to the Department's mandate in PL 96-479, the National Materials and Minerals Policy, Research and Development Act of 1980. In support of the study, the Center is arranging a public Workshop to be held October 1982 on Trends in Critical Material Requirements for Steels of the Future; Conservation, and Substitution Technology for Chromium. The Center serves as alternate to Mr. R. D. Wilson, Director of Office of Strategic Resources, in his capacity as Department of Commerce member of the Federal Committee on Materials (COMAT) and is supporting the Committee in its development of an inventory of Federal Materials R&D for FY82.

Although the majority of the activities of the Center Office are reflected through accomplishments of the Divisions, several of particular interest merit mention here.

The Center coordinated and hosted a Briefing/Workshop on Process Control Sensors for the Steel Industry which was cosponsored by the American Iron and Steel Institute (AISI) and the Defense Advanced Research Projects Agency; the workshop reviewed state-of-the-art technology pertinent to formulating research programs that would address successful development of process control sensors in areas identified by the AISI. It is anticipated that research necessary for development will ultimately be undertaken cooperatively by the steel industry, universities, and government laboratories.

A Congressionally mandated study of the costs of fracture to the U.S. economy was completed by the Center in July 1982. Operational supervision was by Dr. R. P. Reed of the Fracture and Deformation Division.

Center units have participated as organizer, sponsor, cosponsor, or host for the following meetings: (1) Sixth Annual Conference on Materials for Coal Conversion and Utilization, October 13-15, 1981; (2) Deformation, Fracture, Wear, and Nondestructive Evaluation of Materials: Physics and Practice, November 23-24, 1981; (3) Contact Damage in Ceramic Materials at Elevated Temperatures, (cosponsored with the Office of Naval Research) January 21-22, 1982; (4) Thirty-Fifth Symposium of the Mechanical Failure Prevention Group, April 20, 1982; and (5) Seventh International Symposium on Ultrasonic Tissue Characterization (cosponsored with National Institutes of Health) June 6-9, 1982.

Microstructure of Materials  
Task 12101

Although most of the program planning and laboratory activity in the Center takes place in the Divisions, a single task, Microstructure of Materials, in the Center Office, takes a general view of materials science. This task supports cutting edge theory development basic to work in all Divisions and assures adequate attention to major new technical challenges and opportunities, particularly those that may affect two or more Divisions. The task provides senior consultation to the Department of Commerce and other agencies, to other NBS Centers, and to CMS Divisions, and thus provides a window on policy study in the Executive and Legislative Branches.

Fracture Theory  
Subtask 1 of Task 12101

R. M. Thomson

A paper on dislocation screening with Sinclair has appeared in Acta Metall. A second paper with Lin and Weertman has been submitted to Acta Metall. and is now in the review process. In the second paper, the general results on screening from the first screening paper were applied to a continuum, one dimensional model containing an elastic enclave. These results were then applied to fatigue crack growth in metals.

A major review has been prepared on fracture for the new edition of the Cahn-Haasen treatise on Physical Metallurgy. This review treats fracture in a unique way, making use of the fundamental ideas that have been developed here at NBS over the past decade. In this review, a synthesis has been made of the atomic mechanism at crack tips which determine chemical effects and dislocation emission on crack growth with the general screening theory. The general screening theory connects the external response of the system in terms of the screening of the core crack by the dislocation field. The response of the core crack is determined by the atomic structure of the crack tip.

Additional papers are in various stages of preparation. Two are being prepared with Lin on application of screening theory to toughness in metals and on the criterion for dislocation emission. Two papers have been submitted to AIME covering liquid metal embrittlement at an upcoming conference on the same. During this year we have also worked out the early stages of cracks in steady-state motion and on the transformation toughness observed in ceramics.

Theoretical Materials Stability  
Subtask 2 of Task 12101

John W. Cahn

This work addresses fundamental factors in the stability of materials. It is carried on with a wide variety of colleagues.



In support of the phase diagram activity, statistical mechanical calculations of phase equilibria and ordering in hexagonal close packed metals are being carried out. The usefulness of various metastable curves on phase diagrams in predicting sequences of metastable equilibria and phase change mechanism has been explored.

A symmetry theory of crystal-crystal interfaces has been developed and applied to grain boundaries, stacking faults, antiphase boundaries, and solid state phase transformations.

A solid-state thermodynamics theory has been developed which takes properly into account that surface or interface stress is different from surface or interfacial free energy and is being extended to complex crystal structures with complex point defects.

General principles of surface, interface, and grain boundary phase changes have been developed. One important theorem indicates that such changes generally result in faceting to new orientations. Congruent phase changes in which a planar surface change to a planar surface of the same orientation with a new structure occur only for specific, and usually highly symmetric, orientations.

Inclusion or solid precipitates in solid matrices give rise to an elastic distortion whose energy is shape dependent. Shape bifurcations have been shown to occur if interfacial energy is considered.

#### Processes Involving Conformational Changes in Polymers Subtask 3 of Task 12101

Darrell H. Reneker, J. Mazur

The search for improved physical and mechanical properties of polymers has led to the examination of processing methods which combine the effects of crystallization and deformation. In this project, important molecular scale processes associated with crystallographic defects which are created during such processing are identified and quantitatively modeled. The relationships between the behavior of the defects and the macroscopic physical properties are elucidated.

Twist dispiration loops, which both rotate and translate a polymer chain, were shown [1] to provide a molecular scale model that can account for the times associated with dielectric and mechanical relaxation processes. Twist boundaries, composed of partial disclinations, are boundaries where each chain passing through the boundary twists by the same crystallographically determined amount. Twist which accumulates in a chain during crystallization and deformation tends to persist in the chain. Since twisted molecules cannot fit into a crystal, the twisted regions tend to segregate into boundaries which form a template for the processes that result in the establishment of the long period observed in polyethylene fibers. It is necessary for the chains to diffuse along their axes in order to bring free volume to the vicinity of the twist boundaries. Dispiration loops, other crystallographic defects called dislocation loops, and disclination loops participate in this transport process. In order to investigate in detail the conformations and the motions of these defects, energy calculations were performed on defect-bearing

chains inside crystals. Minimum energy conformations and the energetics of defect interactions were determined [2].

Processing by crystallization and deformation produces lengths of straight polymer chains interrupted by folds or other conformational defects. In cooperative work with the University of California and the Science and Education Administration of the Department of Agriculture, the changes in the distribution of straight chain lengths that occur during thermal annealing of lamellar crystals of polyethylene were measured and the results published [3]. It was found that the distribution of chain lengths both broadens and shifts toward longer values during annealing. The behavior of the distribution during annealing was found to be influenced by details of the thermal and mechanical processes by which the samples were prepared.

Molecular transport, which is an essential part of processing and crystallization, is much more complicated than diffusion in low molecular weight fluids because of the large number of internal degrees of freedom of polymer molecules. In collaboration with scientists in the Polymer Science and Standards Division and the Josef Stefan Institute in Ljubljana, Yugoslavia, magnetic resonance measurements of spin echo in a magnetic field gradient are being used to observe the self diffusion of polyethylene molecules in the melt. Current work suggests that polymer self diffusion cannot be characterized by a single time independent diffusion constant. Instead, for diffusion processes, which cover distances commensurate with the dimensions of the polymer molecule, it is desirable to consider a diffusion coefficient which is a function of time. This time dependent diffusion coefficient at short times is much larger than at the long times required to transport the entire molecule. It appears the field gradient NMR method provides a straightforward measure of the spectrum of this time dependent diffusion coefficient.

Small differences in the energy of the various fold conformations available to a crystallizing polymer molecule can have dramatic effects on the morphology of the resulting polymer crystals. Calculations of the conformational energy of folds as a function of temperature, made in cooperation with the Polymer Science and Standards Division, are being correlated with observed changes in the morphology of polymer crystals prepared at various temperatures in order to find processing routes to useful microcrystalline structures. The studies include investigations of fold conformations in multiple fold systems on planes both transverse and inclined with respect to the chain axis. It was found that the fold conformations in multiple fold systems are drastically different from the hitherto investigated single fold systems.

- [1] Reneker, D. H.; Mazur, J. Stochastic defect diffusion model for relaxation effects in crystalline polyethylene. *Polymer* 23: 401; 1982.
- [2] Snyder, R. G.; Scherer, J. R.; Reneker, D. H.; Colson, J. P. Distribution of straight-chain lengths in unannealed and annealed solution-crystallized polyethylene by Raman spectroscopy. *Polymer* 23: 1286; 1982.
- [3] Reneker, D. H.; Mazur, J. Dispirations, disclinations, dislocations, and chain twist in polyethylene crystals. *Polymer*, in press.



Other Activities of the  
Office of the Center for Materials Science

Invited Talks

National Materials Policy: Critical Materials Issues and Opportunities  
1981 Fall Meeting of the Metallurgical Society of AIME, Louisville, KY  
J. B. Wachtman, Jr. and B. W. Steiner  
October 12, 1981

The Symmetry of Martensites  
1981 Fall Meeting of the Metallurgical Society of AIME, Louisville, KY  
J. W. Cahn  
October 12, 1981

Diffusion Induced Grain Boundary Migration  
1981 Fall Meeting of the Metallurgical Society of AIME, Louisville, KY  
J. W. Cahn  
October 13, 1981

Advanced Materials Development: A Technical Response to the Critical  
Materials Challenge  
Sixth Annual Conference on Materials for Coal Conversion and Utilization,  
National Bureau of Standards, Gaithersburg, MD  
J. B. Wachtman, Jr.  
October 13, 1981

Binary Phase Diagram Features Resulting from Higher-Order Phase  
Transitions  
1981 Fall Meeting of the Metallurgical Society of AIME, Louisville, KY  
J. W. Cahn  
October 14, 1981

Symmetry in Solid-Solid Transformation Morphologies  
National Laboratory Inorganic Materials Meeting, Tsukuba, Japan  
J. W. Cahn  
October 20, 1981

Economic Aspects of Fracture  
34th Meeting of the MFPG, Washington, DC  
J. B. Wachtman, Jr.  
October 21, 1981

Wetting Transitions  
Metallurgical Society Meeting, Tokyo Japan  
J. W. Cahn  
October 23, 1981

Diffusion Induced Grain Boundary Migration  
Tohoku University, Sendai, Japan  
J. W. Cahn  
October 27, 1981

Diffusion Induced Grain Boundary Migration  
Nippon Steel, Kawasaki, Japan  
J. W. Cahn  
October 30, 1981

A Crack as a Defect with Implications for Fracture Resistance  
1981 Fall Meeting of the Metallurgical Society of AIME, Louisville, KY  
R. M. Thomson  
October 1981

Symmetry in Solid-Solid Transformation Morphologies  
Japanese Metallurgical Society Meeting, Kyoto, Japan  
J. W. Cahn  
November 3, 1981

Symmetry in Solid-Solid Transformation Morphologies  
Japanese Crystallography Society Meeting  
Fukuoka, Japan  
J. W. Cahn  
November 11, 1981

Alloy Substitution for Strategic Materials  
Sixth Annual Engineering and Technical Conference, Dresser Industries,  
Dallas, TX  
J. B. Wachtman, Jr.  
November 11, 1981

National Needs for Ceramics Research  
Rutgers University, First Organizational Meeting, Center for Ceramics,  
Newark, NJ  
J. B. Wachtman, Jr.  
November 16, 1981

Strain Field of an Inhomogeneous System  
Massachusetts Institute of Technology, Cambridge, MA  
W. C. Johnson  
November 19, 1981

Modern Ceramics Technology  
AAAS Meeting, Washington, DC  
J. B. Wachtman, Jr. and S. J. Schneider  
January 7, 1982

Advanced Materials Development: A Technical Response to the Critical  
Materials Challenge  
California State Polytechnic University, Pomona, CA  
J. B. Wachtman, Jr.  
January 7, 1982

The Motion of Interfaces  
Georgia Institute of Technology, Atlanta, GA  
J. W. Cahn  
January 20, 1982

Materials Issues of Particular Current Interest to the National  
Bureau of Standards and Its Programs Responding to These Issues  
Commission of European Communities in Brussels, Belgium  
J. B. Wachtman, Jr. and B. W. Steiner  
January 26, 1982

The Materials Fracture Research Program at the National Bureau of  
Standards  
NBS-India Workshops on Materials Sciences and Chemical Processing,  
Delhi, India and Bangalore, India  
J. B. Wachtman, Jr.  
February 1, 1982 and February 8, 1982

Defects in Polymers and Polymer Physics  
Fraser Price Memorial Lectures (8), Polymer Science and Engineering  
Department, University of Massachusetts, Amherst, MA  
D. H. Reneker  
February 15-26, 1982 also again April 12-23, 1982

Wetting Near Critical Points  
University of Houston, Houston, TX  
J. W. Cahn  
February 18, 1982

Phase Transition in Metals  
University of California, Santa Barbara, CA  
J. W. Cahn  
March 1, 1982

Interaction of a Dislocation and Precipitate  
Carnegie-Mellon Institute, Philadelphia, PA  
W. C. Johnson  
March 16, 1982

Interaction of a Dislocation and Precipitate  
University of Minnesota, Minneapolis, MN  
W. C. Johnson  
March 17, 1982

Diffusion and Phase Changes in Iron Aluminides  
Wright Patterson Air Force Base, Dayton, OH  
J. W. Cahn  
March 24, 1982

Interaction of a Dislocation and Precipitate  
Los Alamos National Laboratories, Los Alamos, NM and  
University of Utah, Materials Science Department, Salt Lake City, UT  
W. C. Johnson  
March 1982

Interaction of a Dislocation and Precipitate  
Ohio State University, Columbus, OH  
W. C. Johnson  
April 1, 1982

Diffusion Induced Grain Boundary Motion  
General Electric, Schenectady, NY  
J. W. Cahn  
May 14, 1982

Thermodynamics of Surfaces  
Northwestern University, Evanston, IL  
J. W. Cahn  
May 20, 1982

Ceramics Research at the National Bureau of Standards in Support of  
Technology and Industrial Innovation  
84th Annual Meeting of the American Ceramic Society, Cincinnati, OH  
J. B. Wachtman, Jr.  
May 14, 1982

Address to the 1982 Convocation for the College of Engineering,  
Rutgers State University of New Jersey  
Rutgers State University, Newark, NJ  
J. B. Wachtman, Jr.  
May 26, 1982

Ceramics Research at the National Bureau of Standards  
Brazilian Ceramic Society, Recife, Brazil  
J. B. Wachtman, Jr.  
June 1, 1982

The Materials Research Program in the Center for Materials Science  
of the National Bureau of Standards  
CSIR, Pretoria, South Africa  
J. B. Wachtman, Jr.  
June 9, 1982

Advanced Materials Development: A Technological Response to the Critical  
Materials Challenge  
CSIR Pretoria, South Africa and Middleburg Steel Co., Johannesburg,  
South Africa  
J. B. Wachtman, Jr.  
June 11, 1982

The Materials Fracture Research Program at the National Bureau of  
Standards  
University of Cape Town, Cape Town, South Africa  
J. B. Wachtman, Jr.  
June 14, 1982

The Materials Research Program in the Center for Materials Science  
of the National Bureau of Standards  
University of Witwatersrand, Johannesburg, South Africa  
J. B. Wachtman, Jr.  
June 15, 1982



Ceramics Research at the National Bureau of Standards  
CSIR Pretoria, South Africa  
J. B. Wachtman, Jr.  
June 21, 1982

Origin of Long Period Chain Twist Boundaries in Polyethylene Fibers  
and Their Interaction with Point Dislocations  
1982 IUPAC International Symposium on Macromolecules, University of  
Massachusetts, Amherst, MA  
D. H. Reneker and J. Mazur  
July 13, 1982

Dislocation Processes at Cracks  
Gordon Conference on Ceramics  
R. M. Thomson  
August 1982

Twist Boundaries, Long Period, and Crystallographic Defects in Poly-  
ethylene Fibers  
14th Europhysics Conference on Macromolecular Physics, Barcelona,  
Spain  
D. H. Reneker and J. Mazur  
September 24, 1982

#### Technical and Professional Committees and Leadership

Advisory Committee to the Department of Ceramic Science and  
Engineering, Alfred University  
J. B. Wachtman, Jr., Member

Advisory Committee to Materials Research Laboratory, Pennsylvania  
State University  
J. B. Wachtman, Jr., Member

American Ceramic Society  
Rules Committee  
J. B. Wachtman, Jr., Member

American Physical Society  
J. B. Wachtman, Jr., Fellow  
Committee on Applications of Physics  
J. B. Wachtman, Jr., Member

American Society for Metals, International Committee for Phase  
Diagrams  
J. W. Cahn, Member

American Society for Testing and Materials  
D. H. Reneker, Member

Applications in Physics Committee  
Conference on Deformation, Fracture, and NDE, November 1981  
R. M. Thomson and J. B. Wachtman, Jr., Conference chairmen



Committee on Materials (COMAT)

J. B. Wachtman, Jr., Alternate Member

Corporation Visiting Committee, Department of Materials Science and Engineering, Massachusetts Institute of Technology

J. B. Wachtman, Jr., Member

CRC Critical Reviews in Solid State Physics

Board of Editors

D. H. Reneker, Member

Federation of Materials Societies

Committee on Materials Durability and Conservation

J. B. Wachtman, Jr., Chairman

Journal of Resource Management and Technology

B. W. Steiner, Editorial Board

Materials Research Laboratory, University of Massachusetts

Visiting Committee

D. H. Reneker, Member

Materials Coordination Task Force Department of Commerce

J. B. Wachtman, Jr., Member

National Academy of Engineering

Membership Committee

J. B. Wachtman, Jr., Vice-Chairman

National Academy of Sciences

Solid State Sciences Committees

R. M. Thomson, Member

National Archives and Records Service

Advisory Committee on Preservation

D. H. Reneker, Member

Plastics Institute of America

Research Committee

D. H. Reneker, Member

Polymer Science and Engineering

Board of Editors

D. H. Reneker, Member

Study of Critical Materials Requirements of the U.S. Steel Industry

J. B. Wachtman, Jr., Member of NBS team

The Metallurgical Society, American Institute of Metallurgical Engineers

Heat Treatment Committee

J. W. Cahn, Chairman

U.S. National Committee: International Commission for Optics  
B. W. Steiner, Member

Workshop on Chromium and Other Strategic Materials Needs of the  
U.S. Steel Industry  
Sponsors Committee  
J. B. Wachtman, Jr., Chairman

### Publications

Cahn, J. W.; Johnson, W. C. Chemical potentials in solids: a reprise. *Scr. Metall.* 15: 1263; 1981.

Johnson, W. C.; Cahn, J. W. Comment on chemical potentials in solids. *Scr. Metall.* 15: 1259; 1981.

McCrackin, F. L.; Mazur, J. Configuraton properties of comb branched polymers. *Macromolecules* 14: 1214; 1981.

Johnson, W. C.; Lee, J. K. An integral equation approach to the inclusion problem of elasto-plasticity. *J. Appl. Mech.* 49(2): 312; 1982.

Kwon, O'D.; Beaglehold, D.; Webb, W. W.; Widom, B.; Schmidt, J. W.; Cahn, J. W.; Moldover, M. R.; Stephenson, B. Thickness of the liquid-vapor wetting layer. *Phys. Rev. Lett.* 48: 185; 1982.

Piccone, T. J.; Butrymowicz, D. B.; Newbury, D. E.; Manning, J. R.; Cahn, J. W. Diffusion-induced grain boundary migration in the Cu-Zn system. *Scr. Metall.* 16: 839; 1982.

Reneker, D. H.; Mazur, J. Stochastic defect diffusion model for relaxation effects in crystalline polyethylene. *Polymer* 23: 401; 1982.

Snyder, R. G.; Scherer, J. R.; Reneker, D. H.; Colson, J. P. Distribution of straight-chain lengths in unannealed and annealed solution-crystallized polyethylene by Raman spectroscopy. *Polymer* 23: 1286; 1982.

Thomson, R. M.; Sinclair, J. Mechanics of cracks screened by dislocations. *Acta Metall.* 30: 1325; 1982.

Wachtman, Jr., J. B. National materials policy: critical materials and opportunities. *Am. Ceram. Soc. Bull.* 61: 214; 1982.

Butrymowicz, D. B.; Cahn, J. W.; Manning, J. R.; Newbury, D. E.; Piccone, T. J. Diffusion-induced grain boundary migration. Proceedings of the 1982 international symposium on grain boundaries and interfaces in ceramics; in press.

Cahn, J. W.; Johnson, W. C. Where do we go from here? Proceedings of the international conference on solid-solid phase transformation, 1981 August 10-14; Pittsburg, PA; in press.

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#### Honors and Awards

J. W. Cahn  
Fellowship Japan Society for Promotion of Science  
October 1981



## MATERIALS CHEMISTRY DIVISION (561)

Thomas D. Coyle, Chief  
Samuel J. Schneider, Deputy Chief  
Lillian L. Ware, Secretary

Within the overall program of the Center for Materials Science (CMS), the Materials Chemistry Division provides a focus for research and measurement activities which are fundamental to understanding the chemical stability and reactivity of materials in processing and use. The Division provides data, conceptual understanding, measurement methods, standards, and reference materials which find broad application in scientific and engineering activities of industry, other Government agencies, and scientific organizations.

The intrinsic chemistry of materials, and their reactivity with their environment, are critical to processing and to performance and durability in service. The requirements of advanced technology in areas such as transportation, energy, and aerospace for materials that will function at higher temperatures in aggressive environments demand chemically robust materials and the means to assess their performance and extend their service life. National concerns for critical and strategic materials require improved basic understanding of chemical durability to support design and selection of substitutes. Understanding of the chemical reactivity of materials and their degradation products is also critically important to assessing and minimizing the environmental impact of materials processing and use.

The Division's program is broad, in the sense that it addresses chemical aspects of processing, durability, and use of a wide range of materials including metals, ceramics, glass, and polymers. It is tightly focused in the sense that it addresses common problems of chemical behavior of these diverse classes of materials.

The research thrusts of the Division include the following activities:

- (1) Determination of the chemical durability of materials and the mechanisms of degradation, including corrosion and degradation of metals, ceramics, and special-purpose polymeric materials, and chemical aspects of tribology.
- (2) Investigations of the basic chemical phenomena underlying materials processing, including ceramic processing, and production of protective metallic and ceramic coatings.
- (3) Determination of basic mechanisms and measurement methods to control and minimize adverse environmental impact of materials processing and use.
- (4) Development of methods for structural and chemical characterization of materials, degradation products, and process intermediates required to support (1) through (3).

The Division carries out numerous cooperative programs with the private sector and with other Government agencies, providing often unique services to these groups while maintaining the focus of the Division on problems of current technological concern. A long-standing program with the American Iron and Steel Institute (AISI) on corrosion protection of marine pilings was completed this year; the results will provide essential design information for corrosion protection of offshore structures. A joint program with the American Electroplaters' Society (AES) to study new pulsed electrodeposition techniques for producing corrosion resistant alloy coatings has led to new methodology which has the potential for reducing the use of critical alloying elements. A Research Associate program with Mobil Oil has led to development of methods to identify and measure arsenic compounds in shale oil, critical to protection of process catalysts in this area of synthetic fuel technology. Cooperative programs with more than a dozen companies in the petroleum industry have established a basis for quality control assessments of lubricants and oxidation stability.

Joint programs with other agencies provide critically needed data and measurement methods. We have developed for the Federal Highway Administration (FHA) a field instrument to measure corrosion of reinforcing bars in concrete bridge decks. Our research supports the development of new antifoulant coating technology for the U.S. Navy and provides the measurement methods needed to enable the Navy to address environmental impact of this new development. Our ceramic sciences program provides, for example, fluorescence standards to the U.S. Postal Service, data on the properties of structural ceramics for the Department of Energy (DOE), and ceramic processing methodology essential to the development of temperature and oxygen measurement sensors for high temperature applications in steel and energy technologies. Our Glass Group provides tailored glasses for DOE applications in laser fusion research and to support the Department of Defense (DOD) requirements for fiber-optic sensors.

The Division's outputs include major activities in the area of evaluated standard reference data, including production with the American Ceramic Society (ACerS) of the widely-used Phase Diagrams for Ceramists. In FY82, major efforts were made to expand this activity, develop increased industrial support in conjunction with ACerS, and automate the operations of the Phase Diagrams for Ceramists Data Center. A continuing research associate program with the Joint Committee on Powder Diffraction Standards produces standard x-ray powder patterns, and major advances have been made in application of computer techniques for profile analysis and quantitative x-ray powder diffraction analysis. A third data activity has led to completion of a major volume on materials performance data in coal conversion systems.

Production of Standard Reference Materials (SRM) is another major Division activity. We produce 5000 SRM units annually for calibration of coating thickness measurement instrumentation in support of the metals, coatings, and electronics industries. Our dye-penetrant crack SRM, produced by the Electrodeposition Group, is required by the Federal Aviation Administration (FAA) as a basis for inspection of aircraft components. Other SRMs include standards for qualitative and quantitative x-ray diffraction analysis, property standards for control of processing in the glass industry, and compositional standards for particulate and surface analysis.



The present structure of CMS places the major NBS responsibility for ceramic sciences activities in the Division. Accordingly, Division management has undertaken a thorough-going review of our ceramic programs in the context of current thrusts in ceramic sciences and technical and industrial needs. The Division has instituted a systematic series of contacts with the industry, a cooperative assessment of economic and technical aspects of advanced ceramic technology (in cooperation with the NBS Planning Office and the Fracture and Deformation Division), and a formal ceramic program planning activity to determine the directions of future NBS efforts in ceramics and glass.

The research activities of the Division, and its recent technical accomplishments, are described in the following pages. For management purposes, the technical program is divided into task areas, as follows:

Task 12113--CORROSION AND PROTECTION OF METALS. Concerned with the mechanistic and environmental parameters controlling metallic corrosion and the electrodeposition of coatings; major emphasis on corrosion measurement and detection, mechanisms of localized corrosion such as crevice corrosion, stress corrosion cracking, hydrogen embrittlement, development of SRMs for coatings, and processing science related to coating technology.

Task 12114--MATERIALS BIOTRANSFORMATIONS AND CHEMICAL DURABILITY IN SERVICE ENVIRONMENTS. Involves the mechanistic behavior of materials degradation in their service environments, particularly that related to chemical and biological initiated reactions. Major thrusts directed toward microbial corrosion and to the key transport or diagnostic chemical species which define pathways to chemical and biological transformations of materials in service environments.

Task 12115--HIGH TEMPERATURE MATERIALS CHEMISTRY FOR PROCESSING AND DURABILITY. Relates to the thermodynamic and kinetic behavior of materials in aggressive service environments at high temperatures and pressures. Major work directed toward phase equilibria of ceramic/glass systems through modeling and experiment. In cooperation with the American Ceramic Society the widely-used Phase Diagrams for Ceramists, is compiled and edited through the data activities within this Task.

Task 12154--PROPERTIES, STRUCTURE, AND STANDARDS FOR GLASS AND OPTICAL MATERIALS. Concerned with the processes involved in the synthesis, forming, and uses of glass and optical materials, including thin films. Major activities are devoted to the development of SRMs needed by the glass industry and others such as those for viscosity, resistivity, dielectric constant, thermal expansion, and chemical-analytical purposes; optical properties of glass; and process-structure-property relationships in thin films of glasses and ceramics.

Task 12156--CERAMIC PROCESSING AND DURABILITY SCIENCE. Involves chemical and physical processes influential in producing reliable and durable ceramics. Particular emphasis on establishing controlling materials parameters throughout the ceramic processing cycle. Major activities are devoted to powder and compact characterization by

x-ray methods and electron microscopy and structural chemistry aspects at ambient and high pressures and temperatures. X-ray SRMs and standard data are significant products.

Task ----- RECYCLED OIL PROGRAM. Concerned with the development of data base and test methodology for the NBS Recycled Oil Program. Major emphasis on chemical stability of complex organic mixtures at metal-lubricant surfaces, reaction kinetics in condensed phase systems, tribology and tribochemistry, and chemical characterization of lubricant and fuels.

#### FY82 Significant Accomplishments

##### Task 12113--CORROSION AND PROTECTION OF METALS.

- Successful use of a new surface EXAFS technique to demonstrate the noncrystalline structure of the passive film formed on iron in a chromate passivating solution.
- Successful application of the electrochemical corrosion measurement techniques developed by the Corrosion Group to in-service copper concentric neutral cables in Baltimore, MD.
- Sixty-eight steel piles exposed for thirteen years to an offshore seawater environment have been removed and evaluated for corrosion damage. These data are being correlated with data obtained during exposure using electrochemical techniques.
- An instrumented probe designed to simulate heat exchange steam pipes in a refuse burning incinerator has been installed at the NASA-Langley incinerator facility allowing data to be obtained on the corrosion performance of five alloys.
- Techniques have been developed to separate pitting and crevice corrosion phenomena, including an ability to initiate pits in 5 to 60 s that simulate those that develop over months and possibly years. This allows one to determine corrosion rates and study the kinetics of the two systems separately.
- A technique has been developed which allows effective simulation of corrosion processes under organic coatings, leading to design of more effective corrosion control strategies.
- Alloys of nickel containing up to 60 wt. % chromium were produced using a new process developed by the Electrodeposition Group. These coatings can be formed in thick layers. Corrosion and wear performance, along with deposition mechanisms, are currently under study.
- Two new microhardness standard reference materials in the range of 100 khn and 500 khn have been developed. These standards exhibit significantly improved uniformity of hardness over currently available non-NBS standards.



Task 12114--MATERIALS BIOTRANSFORMATIONS AND CHEMICAL DURABILITY IN SERVICE ENVIRONMENTS.

- Development of measurement methods and preliminary data supporting a new mechanism of anaerobic biocorrosion of bulk iron. This will provide diagnostics for economically significant biocorrosion and permit design of more effective corrosion control.
- Incorporation of complementary molecule-specific characterization methods into Mil-Spec development for Navy's major procurement of fleet antifoulant polymers.
- Demonstration of theoretical basis for correlating molecular conformations and shapes to liquid chromatography separations and NMR spectra. This provides a significant new tool for characterization of degradation products and determination of corrosion mechanisms.
- Characterization of a mercury-reducing enzyme imparting toxic metal-resistance in bacteria crucial to bioleaching technology for copper mining.
- Demonstration of the concentration of organotin biocide residues in marine surface water microlayers as a key component in their environmental fate.
- The Mobil Research and Development Corp. has established a research associate program in the Materials Chemistry Division dedicated to ultratrace speciation of arsenic in industrial shale oils and process waters. This work will extend to shale oils the element-specific molecular characterization methods developed by the Chemical and Biodegradation Processes Group.

Task 12115--HIGH TEMPERATURE MATERIALS CHEMISTRY FOR PROCESSING AND DURABILITY

- Volume IV of Phase Diagrams for Ceramists, containing 570 critically evaluated new diagrams of metal-oxygen, metal-oxide, and oxygen-containing radical type systems, was published by the American Ceramic Society. Final editing of Volume V, containing about 750 new diagrams of halide, sulfide, oxynitride, aqueous, and ceramic-gas systems was substantially completed.
- A new theory for mixing of complex liquid and solid phases has been developed and validated (by comparison with experimental activity and phase equilibria data) for representative ceramic, slag, and glass systems containing  $K_2O$ ,  $CaO$ ,  $Al_2O_3$ , and  $SiO_2$ ; and molten salt systems containing  $PbCl_2$ ,  $CsCl$ ,  $PbBr_2$ ,  $NaBr$ ,  $KBr$ , and  $CdCl_2$ .
- Reactions between  $HCl$ -containing gases and glass or dolomite substrates, leading to alkali vapor transport have been shown to be highly rate limited. This indicates that chemical kinetic factors must be included in current thermodynamic modeling efforts for the prediction of alkali vapor transport in coal conversion/combustion systems.

- The effect of particle size on sintering properties (density and strength) of potassium and calcium aluminosilicate phases has been determined, leading to a new synthesis of refractory ceramics with improved density and strength.
- The "continuous" phase transition in  $\text{ZrTiO}_4$ , an important microwave dielectric, was characterized and single crystals containing no superstructure, an incommensurate superstructure, and a commensurate tripled cell were synthesized using various fluxes.

#### Task 12154--PROPERTIES, STRUCTURE, AND STANDARDS FOR GLASS AND OPTICAL MATERIALS

- Using the unique thin film facility at NBS, it has been demonstrated that microstructure of  $\text{ZrO}_2$  films, important as optical coatings, can be modified by vapor codeposition processing incorporating  $\text{MgO}$  or  $\text{SiO}_2$ . By control of deposit composition and process temperature, amorphous films can be obtained, eliminating grain boundaries potentially deleterious to the durability of coatings.
- Six techniques have been compared for measuring thin films of  $\sim 1 \mu\text{m}$  thickness: stylus profiling, dual beam interferometry, multiple beam interferometry, prism-coupler method, ellipsometry, and channeled spectra; they are found to be of comparable accuracy. The prism coupler method has been used also to obtain accurate refractive index and dispersion data for a mixed  $\text{MgO-SiO}_2$  film. Because of the high precision of this method, estimates of the internal stress in films are possible.
- In collaboration with Stanford University, recent work showed that in situ observations of phase separation in the  $\text{BaO-K}_2\text{O-SiO}_2$  system could be monitored by time-resolved small-angle x-ray scattering technique and a high energy (Synchrotron) source.
- Activities leading to the certification of a dielectric constant glass standard (SRM 774) have been completed. This work involved the completion of interlaboratory comparison with industrial laboratories, statistical analysis of data, test methods and procedure improvements, sample preparation for SRM packaging, and issuance of SRM certificate.
- A series of silicate glasses (containing alumina, alkaline earths, and tantalum oxide) have been prepared that have both unusually high Young's modulus ( $E > 1.1 \times 10^{12} \text{ dyn/cm}^2$ ) and as unusually low linear thermal expansion coefficient ( $\alpha < 3 \times 10^{-6}/\text{K}$  at  $20^\circ\text{C}$ ). The two properties make these glasses highly desirable for the production of pressure insensitive optic fibers.

#### Task 12156--CERAMIC PROCESSING AND DURABILITY SCIENCE

- Application of digital data collection and x-ray line profile refinement for powdered materials was a major accomplishment. Accuracy in measurement of  $2\theta$  was demonstrated to be  $\sim 0.03^\circ$ , which is three to



five times better than the average error associated with strip chart recording methods. The profile model developed was shown to be superior to existing functions normally applied.

- The structures of amorphous/glassy materials were determined at elevated pressure for the first time using a radial distribution function analysis technique and the diamond anvil pressure cell.
- $\text{YCrO}_3$ -based, sintered ceramics were specially processed for a unique NDE study. A phase transition associated with a small volume change appears to occur near 1100 °C. This transition induces microcracks that heal and reopen with appropriate anneals. The material serves as a model ceramic for elasticity and small-angle neutron scattering (SANS) measurements to detect microflaws.
- It has been shown that unlike pure  $\text{Al}_2\text{O}_3$ , powders containing  $\text{Cr}_2\text{O}_3$  in solid solution nucleate a considerable volume fraction of the stable  $\alpha$ -form when plasma sprayed. Such ceramic coatings on Mo-substrates are adherent, and preliminary tests indicate excellent corrosion/erosion resistance in molten iron (~ 1550 °C).
- Two instrument 2 $\theta$  calibration standards have been certified: silicon powder (SRM 640A) and fluorophlogopite powder (SRM 675). The latter is a low 2 $\theta$ /large d-spacing standard.
- A major handbook, Construction Materials for Coal Conversion--Performance and Properties Data has been completed. It contains some 800 pages of evaluated corrosion, erosion, and mechanical property data for metals and ceramics tested under coal conversion conditions.

#### Task ----- RECYCLED OIL PROGRAM

- A gel permeation chromatography-graphite furnace atomic absorption apparatus was built to study the role of organometallic reactions in wear contacts. Organic iron compounds formed as a result of wear were associated mainly with high molecular weight oxidized hydrocarbon structures (1,000 to 100,000 MW), were shown to be formed in wear processes--a major advance in understanding of tribochemical processes.
- Significant advances were made in the area of separation science of complex organic mixtures. A novel separation method was developed using neutral activated alumina column and selected solvent systems to separate the naturally occurring polar molecules in fuels and lubricating base oils into their molecular compound classes.
- Two cooperative studies with industry were conducted: (1) An NBS/ASTM basestock consistency program was successfully concluded. Monthly production samples of lubricating base oils were received from 10 refineries (6 re-refined, 4 virgin base oils). Fourteen industrial/government laboratories participated in analyzing these base oils for consistency and performance. (2) A program involving 11 companies was initiated to study the effects of base oil composition on oxidation stability with additives. Over 100 base oils from 10 crude sources were supplied by the companies with analytical data.

Using an NBS developed thin-film oxygen uptake test, it was established that the correlations linking compositional parameters to oxidation stability are statistically significant.

## CORROSION AND PROTECTION OF METALS

### Task 12113

The activities of the Corrosion and Protection of Metals Task are aimed ultimately at reducing the severe economic losses resulting from corrosion. They are concerned with both measurement methodology and establishing the scientific base necessary to support such endeavors. Thus the work carried out includes basic studies of the mechanisms of specific corrosion and electrodeposition processes; the development and evaluation of test methods, both in the laboratory and in the field; the generation of specialized corrosion data; and the development of SRMs. The work is carried out under two subtasks, one dealing with corrosion and one with electrodeposition.

Much of the work in the corrosion subtask is focused on localized corrosion, namely, pitting, crevice corrosion, stress-corrosion cracking, and hydrogen embrittlement. Each of these commonly encountered forms of localized attack involves the breakdown of the protective surface films which normally impart corrosion resistance to engineering alloys. The so-called passive films of the type found on stainless steels are of particular commercial importance, and their structure and breakdown received continued attention during FY82.

The electrodeposition subtask is important to metals processing technology for the production of economical and energy efficient materials and coatings which are unusually resistant to corrosion and wear. Improvement of coatings to enhance the corrosion and the wear resistance of alloys is a major element in strategies to reduce dependence of U.S. industry on critical materials such as chromium. This subtask seeks to develop new understanding of the properties and structures of electrodeposition processes, to improve current electrodeposition technology, to produce and develop SRMs that are necessary for the measurement technology widely used by the coatings industry, and to devise new SRMs, requiring electrodeposition for their fabrication, for use in nondestructive evaluation techniques and for instrument calibration.

The technical activities carried out under each subtask are described below.

#### Corrosion

##### Subtask 1 of Task 12113

J. Kruger, N. K. Adams, U. Bertocci, T. Cassagne<sup>1</sup>, E. Escalante, J. L. Fink, J. L. Mullen, E. N. Pugh, K. A. Rhyne, J. J. Ritter, M. J. Rodríguez, G. Rondelli<sup>2</sup>, B. T. Sanderson, P. W. Slattey<sup>3</sup>, J. Smit, D. K. Tanaka<sup>4</sup>, F. Thomas, Mingda Wu<sup>5</sup>, Yang-Xiang Ye<sup>6</sup>

<sup>1</sup>Guest Worker from "Compiègne" University of Technology, Angoulême, France

<sup>2</sup>Guest Worker from C.N.R. Laboratorio per la Tecnologia dei Materiali Metallici non Tradizionali, Cinisello (Milan), Italy

<sup>3</sup>Guest Worker from South Australian Institute of Technology, Adelaide

<sup>4</sup>Guest Worker from Technological Research Institute of São Paulo, Brazil

<sup>5</sup>Guest Worker from Shanghai Research Institute of Materials, Shanghai, People's Republic of China

<sup>6</sup>Guest Worker from Wuhan Research Institute of Materials Protection, Hankou, People's Republic of China



## Passive Film Properties

The breakdown of passive films is an important factor in localized corrosion. One approach to the study of film breakdown involves the analysis of electrochemical noise. This new method promises to provide a research and measurement technique for monitoring pitting in critical components, and to give fundamental insight into the pitting process itself. In these studies, three Fe-Cr alloys of different Cr content were held under potentiostatic conditions in the presence and absence of pitting-inducing chloride ions, and the amplitude and frequency content of the current fluctuations were examined. In the absence of the chlorides, no current fluctuations were detected for any of the alloys. This is an important observation in itself, since it suggests that the film does not undergo breakdown, in contrast to a widely held view that random breakdown always occurs and that the occurrence of pitting depends on whether repassivation takes place. Thus the present work suggests that the most important role of the aggressive anions is in increasing the chance of local film breakdown rather than affecting the repassivation rate.

In the presence of chloride ions in solution, random spikes in the current, as shown in figure 1a, were observed during the induction period. The corresponding spectra were in general flat, confirming that the current transients have decay times shorter than 10 ms. Once a pit started growing, the current increased in a roughly linear fashion, becoming progressively noisier. The spectra taken during pit growth show decreasing amplitude with frequency, often exhibiting two different slopes on a logarithmic plot. Examination of the slope of the spectra suggests that the repassivation of the exposed areas is a complex process and not a simple exponential decay of the active current. Guest Worker Y. Ye participated in this work.

The observation of time series such as those shown in figure 1a raised the question of whether their statistical analysis would be useful for the construction of models, leading perhaps to a mechanistic interpretation of the random current fluctuations. Finding a suitable statistical model to describe the fluctuations before and during pitting, as well as in other corrosion situations, would also help in deciding which of the possible spectral estimation techniques is more appropriate. Since other workers in the field of corrosion noise have recently proposed the use of the maximum entropy spectral analysis (MESA) method as more suitable than the Fourier transform method, an examination of this issue appears necessary.

Exploratory work aimed at finding out whether a moving average or an autoregressive statistical model better fits the experimental time series was conducted in cooperation with S. D. Leigh of the Center for Applied Mathematics. Also, computer programs were prepared for the purpose of comparing different spectral estimation techniques. Very simple mechanistic models were formulated, so as to generate time series of random fluctuations to be used for statistical modeling. For instance, figure 1b derived from a model based on the assumption of randomly occurring active areas on a passive electrode, which then repassivate according to various time functions, can predict fluctuations very



similar to those shown in figure 1a. Testing of such models was initiated. Computer simulations were also used to study the effects of the measurement techniques on the statistical structure of the experimental data.

Three other studies of the passive film on iron and ferrous alloys were initiated during the year. The first was directed at gaining an understanding of a new treatment for Type 304 stainless steel which has been claimed to produce a more resistant passive film. This is a particularly intriguing possibility since Type 304 steel is the workhorse of corrosion resistant materials, despite its propensity to localized corrosion. According to a recent report from the Shanghai Research Institute of Materials, this improvement was obtained by anodizing the steel in dilute sulfuric acid in the transpassive region. The precise details were not available, but a general study was made of the growth of anodized films in the transpassive region, primarily using ellipsometry and impedance techniques. Guest Worker G. Rondelli collaborated in these studies. The results indicated that drastic changes in the optical and electrical properties occur in a very narrow potential range. In the potential region where anodization is supposed to improve corrosion resistance, it was found that a thickening of the oxide film occurs. However, the ac impedance results point to an increase in corrosion resistance due to a slowing of the charge-transfer resistance rather than to a film thickening. Capacitance increases can be interpreted as due to adsorption of ions, perhaps hexavalent Cr. It should be noted that surface analyses carried out on the anodized film showed a ten-fold enrichment in Cr as compared with the bulk metal.

The second study is concerned with the structure and nature of the passive film on iron. It is a collaborative research effort with G. G. Cohen and M. Kuriyama of the Metallurgy Division and seeks to provide structural and compositional information on passive films on iron and the changes that take place in these films during breakdown. This information is of great importance to our understanding of all localized corrosion processes which usually involve as a first step the breakdown of passivity. This collaborative study involves a new and very sensitive surface, extended x-ray absorption fine structure (EXAFS), technique developed by NBS. During the year, this work has revealed that the passive films formed on iron exposed to chromate and nitrate passivating solutions have higher percentages of covalent bonding, especially the chromate, and have structures different from the known crystalline iron oxides or oxyhydroxides. Around 12 percent of chromium, a glass former, was found in the films formed in chromate which were more glassy than the films formed in the nitrate solution.

The third study on passivity concerns the formation and breakdown of passive films on steel in ethanol, a problem of importance to the use of ethanol as a motor vehicle fuel. This work is a collaborative effort between Guest Worker D. K. Tanaka and Division 561 personnel. Its main approach has been to use ellipsometric measurements to follow passive film formation and breakdown. This is necessary because electrochemical measurements are not very useful in the low conductivity ethanol solutions. Electrochemical noise measurements were also carried out. The studies have shown that only slow oxide film growth is observed in 95 percent ethanol in the presence or absence of chloride ions. Only when a low

level of contaminants, such as an acid ( $\text{H}_2\text{SO}_4$ ), is present does dissolution of the air-formed film and roughening of the surface occur.

### Pitting and Crevice Corrosion

Pitting corrosion involves both the initiation and growth of pits. The studies described above have focused primarily on the initiation stage, i.e., film breakdown, and on the nature of the film. In another major effort, attention was directed to the growth stage, specifically to the determination of quantitative values of pit growth rates as a function of potential and temperature. In addition to obtaining a better understanding of the growth mechanism, our interests here are on long-term prediction and accelerated testing, currently a special concern of a number of critical technologies such as the development of reliable systems for the storage of nuclear wastes. Guest Worker M. Wu collaborated in these studies, which were carried out on Type 304 stainless steel in 3.5% NaCl solution, a system in which localized corrosion occurs readily.

To study the growth process, it was first necessary to reduce the incubation period for pit initiation, usually quite long. Other workers have achieved this by laser damage or drilling, but this is not thought to simulate normal pit initiation. Thus, an electrochemical technique was developed for this purpose. First it was necessary to determine the pitting potential,  $E_p$ , below which pits are not initiated, and the protection potential,  $E_{\text{prot}}$ , below which pits, once initiated, no longer propagate. This was achieved by cyclic potentiodynamic methods. Once these potentials were established, pits were initiated potentiostatically by rapidly increasing the potential above  $E_p$ , and the potential was then rapidly reduced to a value between  $E_{\text{prot}}$  and  $E_p$ , permitting the pits to grow. (Note that  $E_{\text{prot}} \leq E_p$ .) This procedure, which has now been adopted at Brookhaven National Laboratory (BNL) and by other groups, allows one to initiate pits in 5 to 60 s with similar chemical and mechanical properties to those of naturally occurring pits that take months and years to form. The growth of the pits was studied by monitoring the current as a function of time in the potentiostatic tests. Several potentials and several temperatures in the range 0 to 45 °C have been studied so far. Interestingly, the preliminary results indicate that the pit growth rates are greater at 25 °C than at either 0 °C or 45 °C.

These studies are being extended to crevice corrosion, a process which also involves the breakdown and repair of the passive film and which is commonly believed to be closely similar to pit growth. A specimen configuration has been developed and initial tests are in progress. Tests will be conducted at the same potentials and temperatures as in the pit growth experiments, permitting direct comparison.

### Stress-Corrosion Cracking

Another major effort involves stress-corrosion cracking (SCC). In this case, the passive or protective films are broken by stress, permitting the environment to interact directly with the underlying metal. The



nature of the interaction which leads to cracking remains poorly understood, despite the fact that SCC continues to limit the performance of virtually all engineering alloys. Effort is divided into the development and evaluation of test methods to determine SCC susceptibility and studies of the basic mechanisms of failure. In the former, further attention has been given to the load-pulsing technique for measuring the velocity of stress-corrosion cracks. In this method, small load pulses are periodically applied to a specimen undergoing cracking under an otherwise constant tensile load. The pulses cause limited crack blunting which produces markings on the resulting fracture surfaces, corresponding to the successive position of the crack front; the crack velocity is obtained from the spacing between the markings and the time interval,  $\Delta t$ , between pulses. This method offers a convenient and inexpensive way to obtain crack velocities. However, it is important to demonstrate that the pulses do not influence the velocity. In our earlier work on Type 310 austenitic stainless steel in an aqueous chloride solution, it was shown that the Stage II velocity, i.e., corresponding to the stress-independent region of the velocity-stress intensity relationship, was independent of the magnitude of  $\Delta t$  over a wide range of values. Over the past year, Guest Worker P. W. Slattery and Division 561 personnel extended these studies to the transgranular SCC of Admiralty Metal in aqueous ammonia, a system of considerable practical importance, e.g., the failure of condenser tubes. Again the Stage II crack velocity was found to be constant for a wide range of values of  $\Delta t$ , figure 2. The velocity can be seen to increase progressively as  $\Delta t$  decreases below  $\sim 100$  s, and this is considered to result from a fatigue contribution to crack extension. The constant value,  $\sim 2 \times 10^{-7} \text{ m}\cdot\text{s}^{-1}$ , is in good agreement with those obtained by conventional methods. It is planned to extend this method to studies of the effect of temperature on crack velocity.

The mechanistic studies have been focused on copper and alpha-phase copper alloys. The failure of Admiralty Metal and Cu-30Zn in aqueous ammonia is of particular interest mechanistically because of the ongoing debate on the role of hydrogen in SCC. Because of the relative mobility of the brasses and the high pH of the ammoniacal solutions, hence a low reversible hydrogen potential, it appears that hydrogen absorption can be ruled out in this system, and, because of similar characteristics, in other important alloys, e.g., austenitic stainless steels. The apparent elimination of a hydrogen model has led to a search for alternative mechanisms. Selective dissolution of zinc has been proposed and much of our effort over the past year has been directed to the evaluation of this possibility for the case of transgranular SCC, shown by our earlier work to involve discontinuous cleavage. It has been proposed that dezincification at the crack tip leads to vacancy injection and that resulting vacancy-dislocation interaction in the plastic zinc permits limited cleavage to occur. To test the feasibility of this proposal, attempts have been made to simulate the proposed crack-tip conditions in purely mechanical tests. Specifically, severely cold worked Cu-30 Zn specimens both poly- and monocrystalline, have been annealed at temperatures below that required to cause recrystallization, permitting various amounts of recovery, a process known to involve vacancy-dislocation interaction; the specimens were then fractured by impact in room temperature air. In other tests, severely cold worked monocrystals were strained to failure at slow strain rates at various temperatures below the recrystallization temperature in dry argon gas. No cleavage was produced in

either set of tests, all specimens failing entirely by ductile processes. Interest in the possible role of dezincification led us to continue our studies of the cracking of pure copper in aqueous sodium nitrite. Extensive efforts, again involving Guest Worker P. W. Slattery, failed to substantiate the report by other workers that cleavage-like SCC can occur in the pure metal. Thus, despite the absence of direct experimental support, the dealloying hypothesis cannot be eliminated as a possible mechanism.

An important development during FY82 was the initiation of a program to mathematically model the environmental conditions within cracks and crevices. This activity began with a study of cracks in the brass-ammonia system, and supported the view that the potential and pH at the crack tip cannot permit hydrogen absorption. These studies are being extended to crevices in iron in caustic solutions, and it is anticipated that the modeling will be followed by experimental studies.

### Corrosion Processes Under Protective Coatings

The studies of the local chemistry in cracks and crevices relate directly to our on-going investigation of the corrosion of painted metals. This program, partially supported by the Office of Naval Research (ONR), has focused on the micro-environment that forms under paints and the passive film formation and breakdown processes that occur in this environment. Besides its contribution to a better understanding of localized corrosion, this project also develops techniques that contribute to the development of more effective corrosion protection by improved organic coatings.

Two approaches have been taken in the investigation of corrosion on painted metals: (1) detection and analysis of subcoating phenomena during corrosion; and (2) an elucidation of the subcoating chemistry responsible for these phenomena. In the first, in situ ellipsometric-electrochemical studies of corrosion of iron and steel protected by organic coatings have been continued. While earlier work treated only the iron/cellulose nitrate system, more recent investigations have included both iron and steel coated with other materials such as polybutadiene and proprietary acrylic lacquers. Ellipsometric responses for specimens undergoing corrosion were quite different for coatings cured at room temperature and those cured at elevated temperatures. An automated ellipsometric system developed for this work provides optical data in much greater detail than possible heretofore. Our interpretation of these new data shows, for the first time, the temporal evolution of subcoating events for the cathodic coating delamination process. These results are summarized graphically in figure 3. In the previous report we speculated that "... changes in the nature of the metal surface 'oxide' films ... can result in bond fracture." The new results clearly show a thinning of the surface "oxide" as the first step in the subcoating events as corrosion propagates. For the systems studied, we propose that dissolution of the oxide film to which the coating is bonded is the predominant mode by which coating delamination occurs. Dissolution of air-formed surface "oxide" films in strong NaOH solution (i.e., a simulated subcoating environment) can be demonstrated independently. The subsequent subcoating events of surface roughening and oxide film thickening are consequences of the dissolution of exposed



metal in strong base and the barrier properties of the delaminated coating, respectively. While the above interpretation applies to coatings cured at room temperature, the ellipsometric responses for coatings cured at elevated temperatures are more complex and are still under analysis.

In the second approach to this problem, a new method for investigating subcoating chemistry has been initiated. A technique which simulates the subcoating corrosion system in the generation of segregated anodes and cathodes has been developed. Preliminary investigations of the chemistry of the anolyte and catholyte indicate the buildup of chloride ions at the anode and high levels of sodium and hydroxyl ions at the cathode. The results are consistent with measurements made on actual subcoating liquids.

#### Test Methods and Corrosion Data for Specific Practical Applications

Work in this area in FY82 has emphasized such diverse but technologically important environments as soils, the sea, waste incinerators, and concrete bridge decks. Significant technical activities during FY82 in have been the following:

(1) The ever-increasing use of buried electric power cables has been plagued by unexpected corrosion problems. Such problems require measurement techniques that allow power company personnel to detect and measure the corrosion of cables without excavation. The Electric Power Research Institute (EPRI) has asked NBS to develop such in situ measurement techniques. This project has been directed in the past year toward field measurements of cables in service and completion of the microprocessor system. The limited number of measurements at four sites in Baltimore, MD, revealed that the corrosion rates measured undergo considerable change with time, making it difficult to clearly identify any given area of cable as a high corrosion area. For purposes of this study it was considered prudent to increase the number of measurements thereby improving the statistical confidence of the results prior to excavation of the cables for verification of our measurements. In addition, three new sites in Baltimore have been identified as high corrosion areas and are now included in our study. The data gathered indicate that the corrosion observed is not generally related to the resistivity of the soil. Of the two original sites identified as suspected of being highly corrosive, our measurements indicate that one of these generally does display high corrosion rates as compared to the other sites. At the second area suspected of having a high corrosion rate, our measurements indicate that the rate does vary considerably with time. The two low corrosion sites do, in general, indicate low corrosion rates as indicated by our measurements. In all cases, the electrochemical polarization measurements are carried out without any significant ac interference. The length of cable undergoing polarization is 5 to 7 meters long with the counter electrode 1 meter from the cable.

(2) The study on the corrosion of metals and alloys used or under consideration for use in waste-to-energy systems supported by the Department of Energy and the Department of Defense was continued. This study is directed toward corrosion problems that may exist in incinerator

systems where refuse-derived fuels are burned. During this year a corrosion probe has been developed and installed at the NASA-Langley incinerator facility in Hampton, VA. This probe (see fig. 4) is air cooled to simulate the surface temperatures of the steam boiler heat exchange tubes, and exposes five ferrous alloys used in incinerators. Four thermocouples are located along the length of the probe providing information to a controller regulating an air valve which controls a flow of air through the probe maintaining it at some preset temperature. The five ferrous alloys are in the form of 1 in. dia., 1 in. long tube specimens which can easily be removed or replaced for inspection. The data indicate that the temperature of the probe can fluctuate from 300° to 750 °F. This is a much wider change than expected. Specimens from this probe were removed for inspection during July. A second probe was also installed at the Wright-Patterson Air Force Base incinerator.

(3) The final phases of an American Iron and Steel Institute sponsored investigation of the effectiveness of corrosion protection of steel piling in seawater by a variety of systems and of methods for evaluating the degree of protection with time were carried out during the past year. Sixty-two H-piles and 6 pipe piles each 35 feet long and weighing almost 1 ton were shipped to Bath, PA, for sandblasting prior to our physical measurements used for evaluating the degree of corrosion deterioration suffered during their 13-year exposure to an off-land ocean environment. The preliminary evaluation revealed that the sacrificial anodes had reduced the extent of erosion damage at the sand/water interface, a region which is otherwise extensively attacked. The large mass of data gathered this year and in years past are now under analysis. The results of this study will provide important engineering data for the design of offshore structures.

Four pilings were extracted the previous year from the underground test site in Montreal, Canada. Three of these piles were removed from their vertical position where they had been driven 12 years before. The fourth pile was removed from a horizontal position approximately six feet below ground. Analysis of the corrosion data clearly indicates that the horizontal pile underwent severe corrosion as compared to the vertical piles. One of the vertical piles was capped with concrete during the exposure period. Some corrosion did develop below the concrete cap but was not as extensive as that which was found at the ground water line. These data too are undergoing further analysis.

(4) An increase in underground telephone cable installation by the telephone industry throughout the United States has created a demand for comprehensive and reliable information with respect to the corrosion of shielding materials. In order to obtain such corrosion data on both currently accepted and proposed experimental cable systems, the National Bureau of Standards and the Rural Electrification Administration initiated a long-term underground corrosion program. This work has been recently described in NBSIR 82-2509 entitled Corrosion Evaluation of Underground Telephone Shielding Materials. Forty-eight systems exposed for periods ranging from 1 to 6 years at 6 different test sites are described in detail, and 12 are not recommended for use. Another 13 are indicated as failing when coupled to copper at one or more of the test sites. The remaining 23 developed varying degrees of corrosion which may warrant



further study. One of the systems, System 65, which is a polyolefin polymer coated aluminum alloy shield bonded to the outer jacket performed well at all sites even after 6 years of exposure. A new updated report is now being completed.

(5) The corrosion of reinforcement bars in concrete bridge decks caused by the use of deicing salts has been estimated by the Environmental Protection Agency (EPA) to cost the economy more than \$200 M annually. Efforts to control this corrosion of steel in chloride contaminated concrete using new protection techniques being developed by Government and industry have been hampered by the lack of a nondestructive method for measuring the corrosion rate of steel in concrete. This measurement of corrosion would allow an evaluation of the effectiveness of the various protection systems. During the past year this project, which is under the sponsorship of the Federal Highway Administration, has extended previous laboratory measurements to an in-service bridge deck located in Virginia off the Washington, DC beltway and to a nearby new bridge that was not yet open to traffic. The in-service bridge was of particular interest because it was widened 2 years before our measurements were made. The corrosion rates measured on the older original center section were similar in magnitude to those measured on the newer sections located on either side. That is, the steel in the newer concrete was corroding at essentially the same rate as that in the older concrete. The older section was over 10 years old while the newer section, as mentioned, was slightly over 2 years old. However, the corrosion rate measurements were found to be much lower on the new bridge not open to traffic. This new bridge which was also about 2 years old had not been salted in the winter. Development of the microprocessor system for making these corrosion measurements is near completion.

#### Electrodeposition

##### Subtask 2 of Task 12113

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The processing and SRM activities of the Electrodeposition subtask have involved the following:

(1) Coatings of nickel chromium alloys have been produced by both dc and pulsed electrodeposition technology. The composition of the alloy can be varied from about 0.2 wt. % chromium up to 64 wt. % chromium and is controlled solely through the deposition parameters (not through changes in the electrolyte composition). The coatings can be produced crack-free in layers whose thickness is only limited by the deposition times. The significance of this result is that the nickel-chromium alloys should be extremely corrosion-resistant (see fig. 5) and at the same time show good wear properties. The characterization of coating has yielded the optimal pulsed deposition processing parameters to produce

smooth crack-free alloys. This project is supported in part by the American Electroplaters' Society and shows promise of providing a commercial technique to deposit corrosion resistant stainless steel coatings. A patent application has been filed for this process.

(2) A project on the electrodeposition of glassy alloys based on the nickel-cobalt-phosphorus-boron family has been underway for three years. It was found in collaboration with Division 564 that the wear resistance in the dry sliding ring on block geometry is comparable or superior to hard chromium. The nickel-phosphorus coatings can be produced by deposition processes that do not present the severe environmental problems associated with deposition of hard chromium. The current efficiency for the deposition of these metallic glassy alloys is about 50 percent, compared with about 11 percent for chromium. It was shown that the nickel-phosphorus metallic glass alloys not only exhibit two distinct local structural configurations for a given composition, but also that the configuration (phase) can be selected electronically through the pulse timing used in the deposition process. It was also shown that the structure exhibiting the greater Knight shift exhibits a discontinuous transformation to the structure with the lower Knight shift. Measurements have been extended to alloys containing up to 42 wt. % phosphorus. No other processing technique has yet succeeded in producing such a wide range of compositions. The practical significance of the work on these metallic glass coatings is that they have been shown to be extremely corrosion-resistant in chloride environments and, unlike metallic glass ribbons, these alloys can be economically applied as coatings to protect against corrosion and even electroformed into large structures. An EXAFS study of the nickel-phosphorus system is now underway. We are also investigating the effect of high pressure on the transformation of one glassy phase to another with Dr. Stanley Block of Division 561. It should be noted that several industries in the private sector have continued our development work on the nickel-phosphorus systems, including Bell Laboratories, Lawrence Livermore Laboratory, and the Utilite Chemical Company.

(3) The industries using or producing coating material particularly the aerospace industry, require means to calibrate their coating thickness measurement systems. Work continued in the production of coating thickness SRMs that industry requires for the calibration of coating thickness gauges. A single SRM is a metal coupon, 3 x 3 cm or 1.5 x 1.5 cm, one side of which has an electrodeposited coating of certified thickness. Most of these are non-magnetic coatings on steel, but also included are nickel, gold, and tin coatings on various metallic substrates. Some 53 different SRMs are available ranging in thickness from 0.7  $\mu\text{m}$  to 2 mm. (Gold coatings are actually certified in units of mass/area, not length.) These standards are designed for use with either magnetic type or beta backscatter type thickness gauges. The SRMs are packed in sets and the SRM catalog lists some 31 different sets. About 4000 individual coating thickness standards were produced during FY80 and about 4700 were produced during FY81. New standards of very thin gold are under development in response to requests by industry.

(4) In response to a request from the Offices of Standard Reference Materials and Nondestructive Evaluation, we have developed two new



microhardness standard reference materials, one of 100 kg/mm<sup>2</sup> and another about 500 kg/mm<sup>2</sup>. The main problems with the standards now available from the makers of the microhardness instruments are typically (a) the lack of uniformity of hardness across the surface, and (b) the lack of a certified hardness. The hardness nonuniformity is a result of inhomogeneities in cooling rate and the resultant composition, inhomogeneity, and grain size variation. Electrodeposition technology allows almost an atomic control of structure and composition. We have succeeded in fabricating hardness SRMs of significantly improved hardness uniformity. These will be made available through the Office of Standard Reference Materials some time next year. Research in this area is continuing to extend the range of hardness to over 1000 kg/mm<sup>2</sup> so that a complete set of standards will be available. We have had a number of requests from industry for Rockwell hardness standards and production feasibility will be evaluated next year.

(5) To enhance productivity and efficiency, the Division has embarked on a program to automate the production of standard thickness SRMs. The automation procedure has been divided into three one year phases. The first is concerned with the implementation of computer compatible measuring instruments which is near completion. The second is concerned with the development of computer software and fabrication of an automatic SRM translation and measuring instrument, and the third with final refinement of the computer software to include statistical analysis, label printing, and inventory control. The x-ray fluorescence instrument used for measuring the thickness of very thin gold and nickel SRMs has already been connected to a computer and the other parts of the automation process are ahead of schedule.

(6) A research project dedicated to improving the accuracy of the x-ray fluorescence thickness measurements is underway. This project has yielded a set of greatly improved operating parameters for x-ray fluorescence thickness testing. Further refinement next year will facilitate the production of new very thin gold standards which have now been requested by industry.

(7) As a part of a cooperative program with DOE to investigate coatings on fuel cell heat exchangers which have to be resistant to very hot phosphoric acid, the Division is measuring properties of a number of different types of electrodeposited coatings including electrodeposited metallic glass alloys, titanium, and titanium diboride, all on copper substrates. This project has just started; however, a number of nickel phosphorus metallic glass coatings have been produced on copper substrates in geometries suitable for corrosion testing.

(8) Dye penetrant crack SRMs have been in production for two years and last year more than 100 were made. This SRM is fabricated using electroforming technology and consists of alternative layers of copper and nickel. There are four layers of copper: the thickest is nominally 2  $\mu$ m, then next 1  $\mu$ m, followed by 0.5  $\mu$ m and 0.2  $\mu$ m. These copper layers are then electrochemically removed and the space that the copper occupied constitutes the crack. A research project was undertaken to improve various unsatisfactory manufacturing techniques and to investigate several important aspects of the crack geometry that have a bearing on

dye pick-up and apparent crack width. Among the topics that were examined were: (a) the extent to which the crack edge was "rounded" by the etching procedure; (b) the depth to which the crack penetrated into the block; (c) the polishing technique which was known to "smear" the nickel over the copper; and (d) various techniques to automate the production process. In order to eliminate as much as possible the rounding of the crack, an improved etching technique was developed and the polishing procedure was changed to reduce to the maximum extent possible the smearing of the nickel. The depth of the crack was also measured. This project is quite important as the Federal Aviation Administration is mandating the use of our dye penetrant crack blocks for use in the inspection of commercial aviation (wing spars, landing gears, etc.). This requirement has necessitated a significant increase in commitment of manpower to the production of this SRM. We anticipate producing from 300 to 500 of these standards next year.

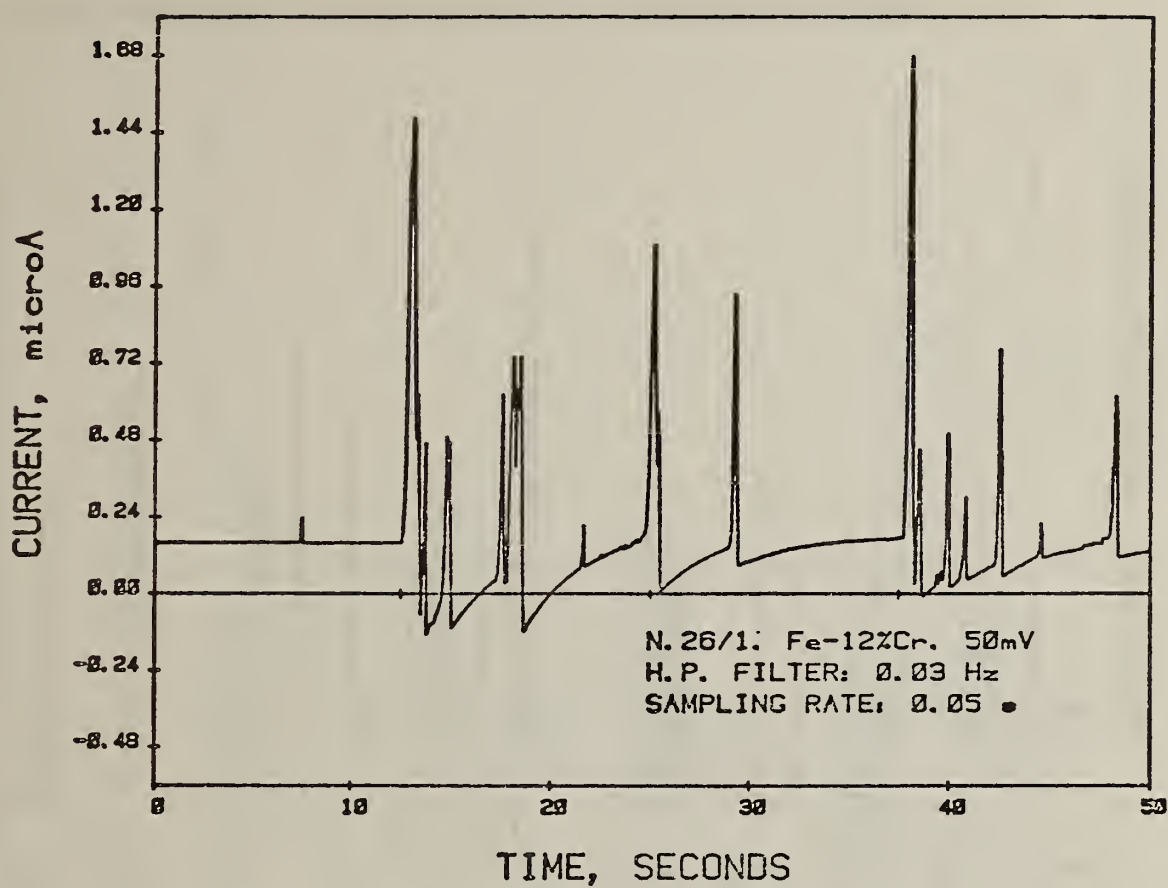


Figure 1a Current fluctuations observed during the induction period leading to the pitting of a Fe-12% Cr alloy.



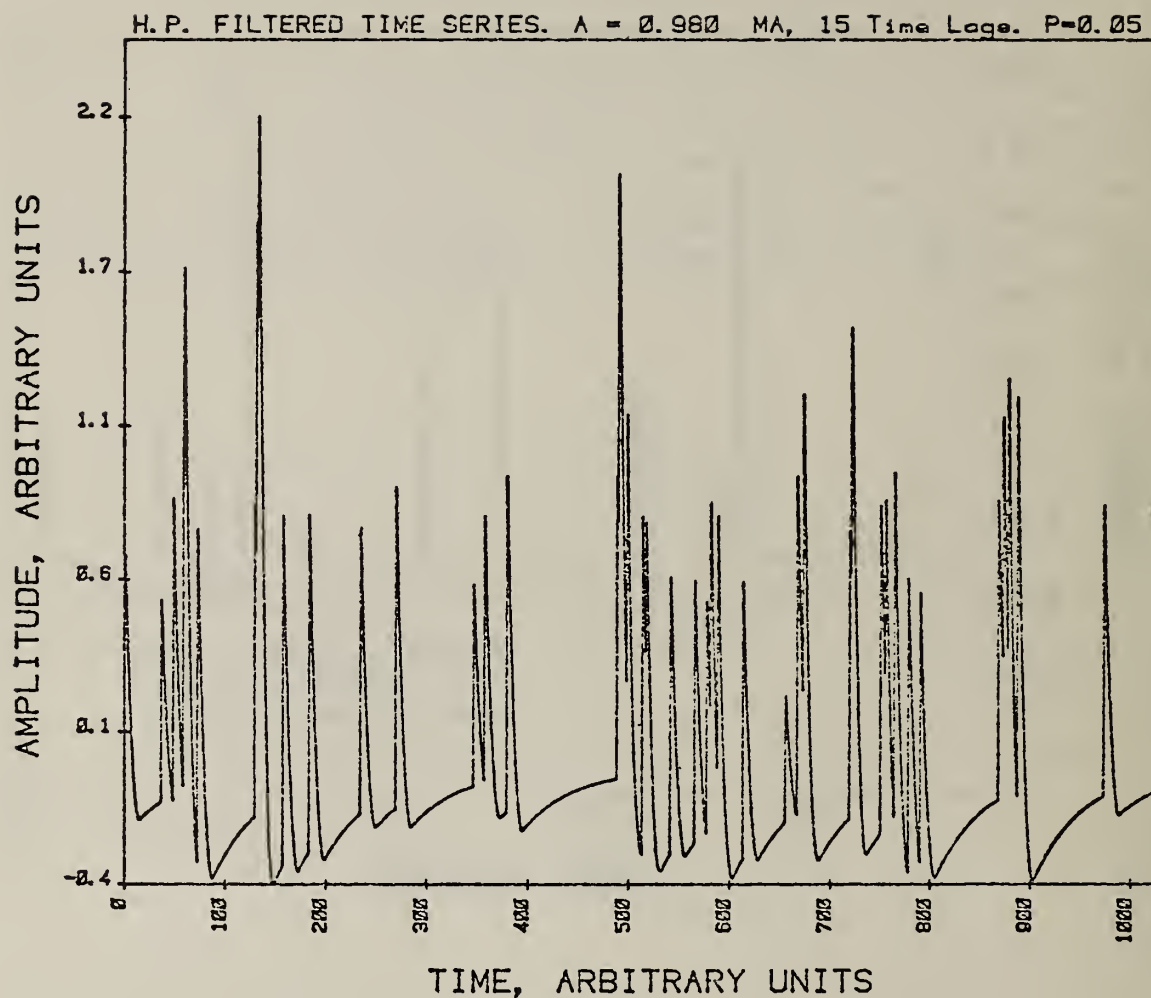


Figure 1b Time series of random current fluctuations calculated from a model assuming random-occurring active area on a passive electrode when they repassivate according to various time functions.

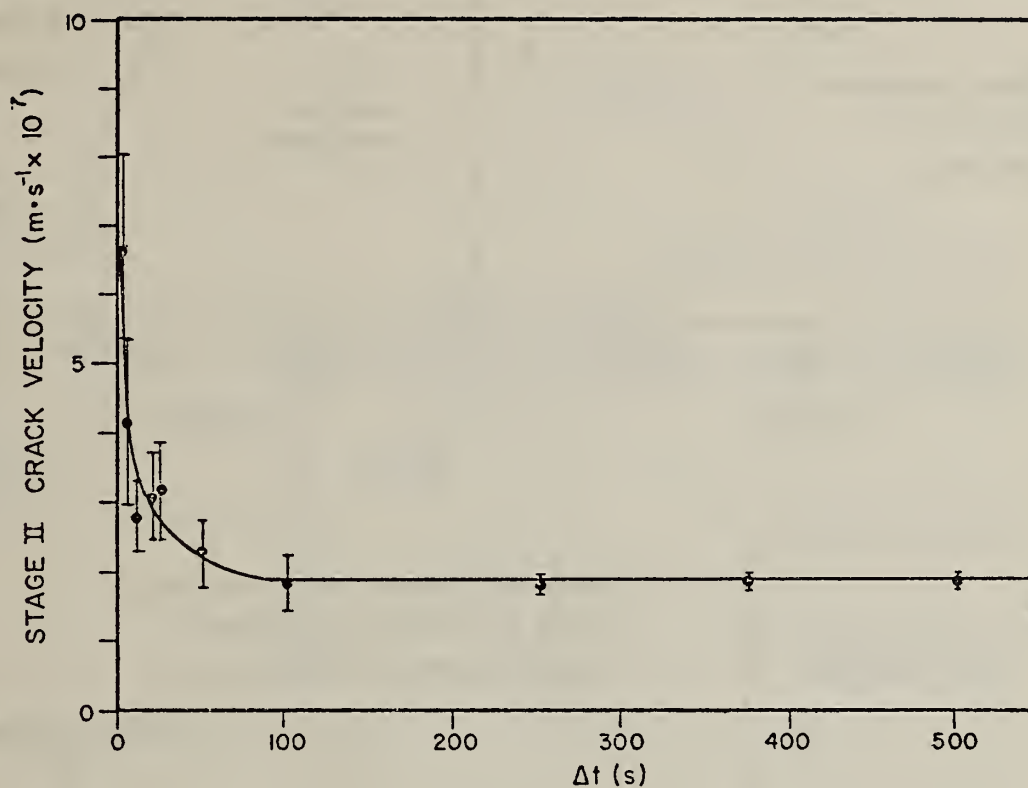


Figure 2 Data for load-pulsing experiments used for determining the velocity of stress-corrosion cracks. These results for Admiralty Metal in aqueous ammonia indicate that the velocity is independent of the time interval between pulses,  $\Delta t$ , over most of the range studied.

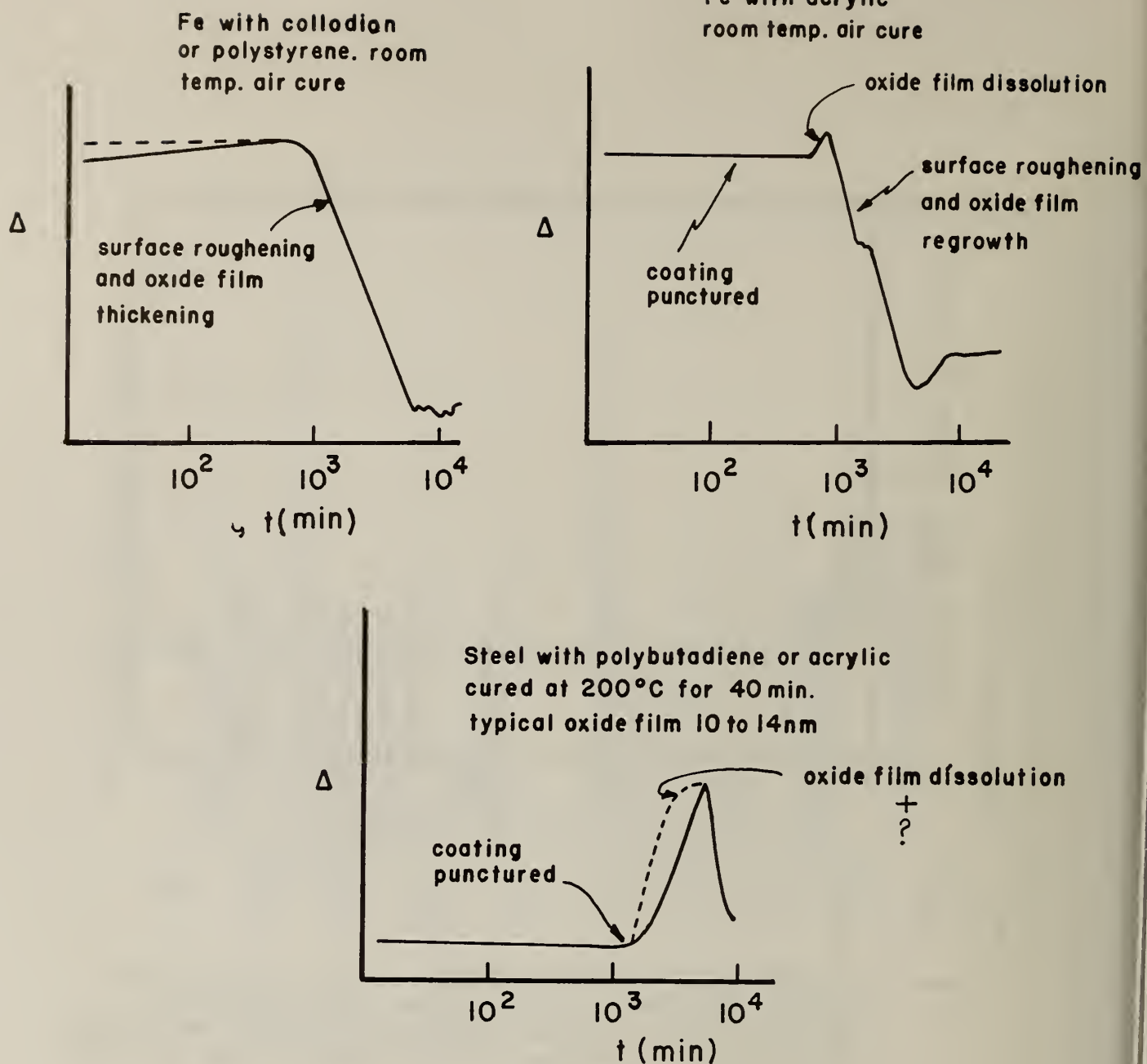


Figure 3 Effect of type of polymeric coating on the ellipsometric measurements of coated iron immersed in sodium chloride solution.  $\Delta$  = phase change of the elliptically polarized light. It is usually related to film thickness or surface roughness.



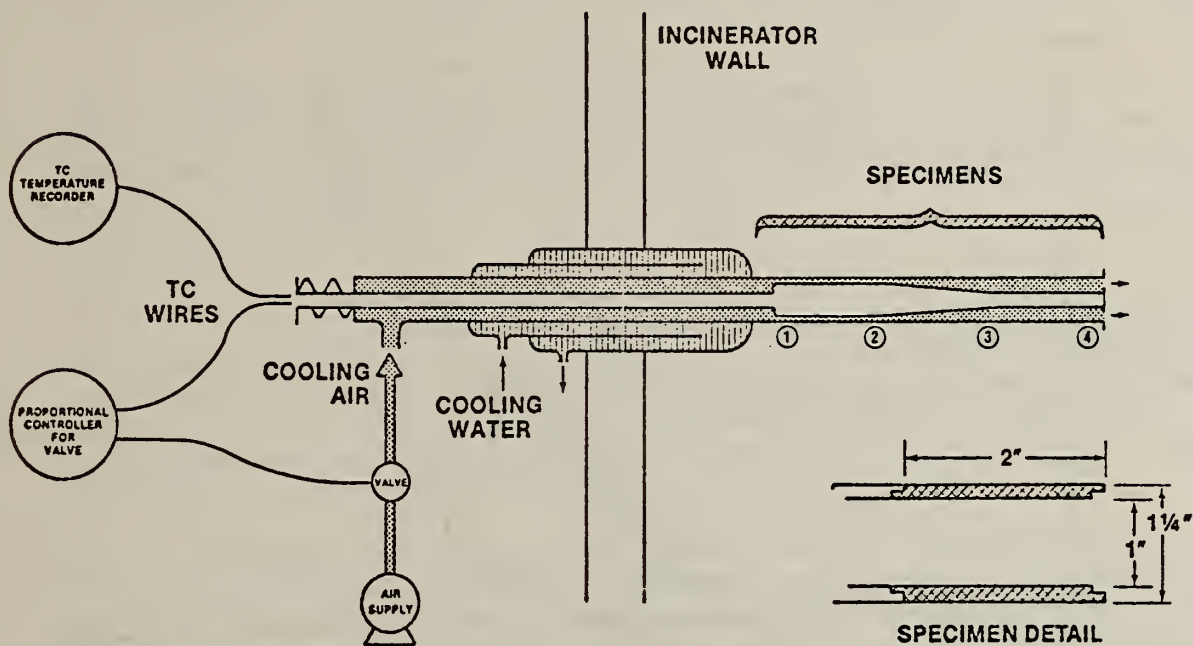


Figure 4 RDF-fired incinerators.

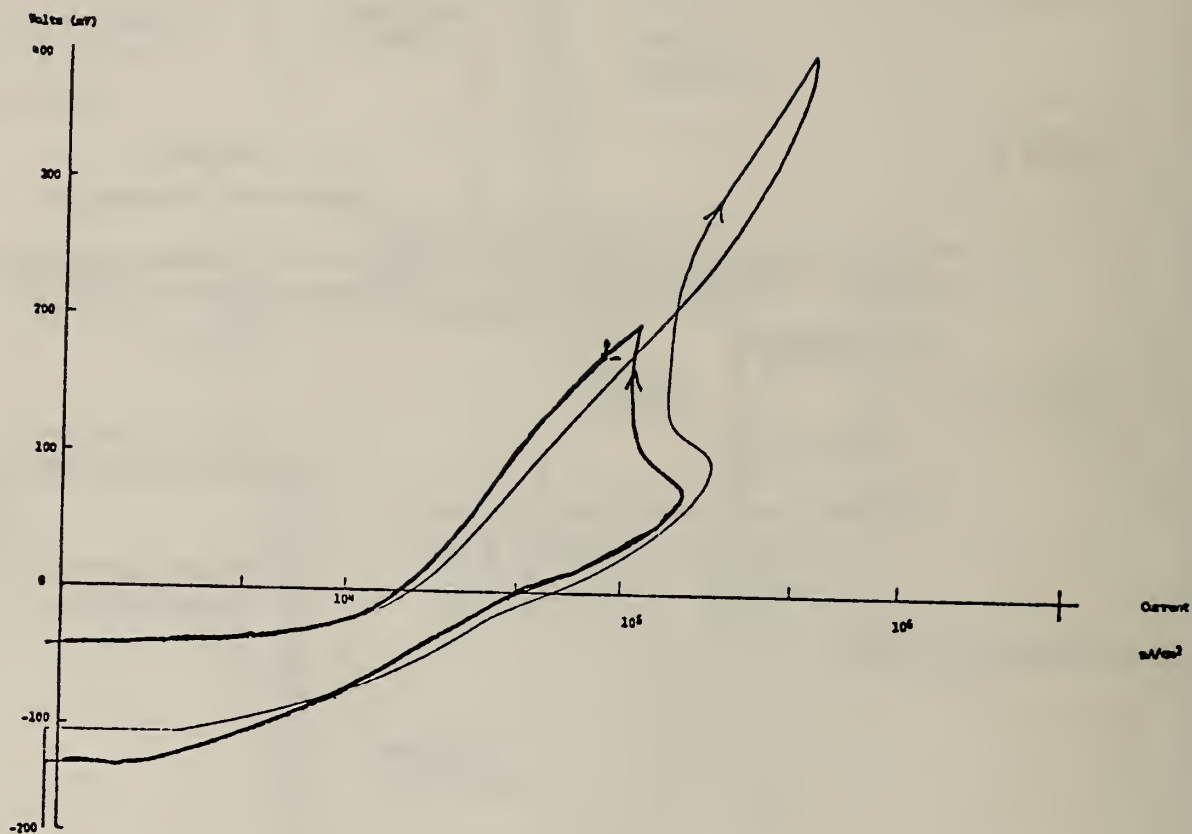


Figure 5 Anodic potentiodynamic voltammetry of a Ni 20 Cr pulsed electro-deposited alloy in a 3.5 wt. % NaCl solution. Heavy curve, -200 mV to +200 mV; light curve, -200 mV to +400 mV. Both curves show regions where passive protective films are formed in the Ni-Cr alloy (e.g., the vertical portions of the curves where the current remains relatively constant with an increase in potential). The lower the value of this passive current, the more protective is the passive film.

MATERIALS BIOTRANSFORMATIONS AND CHEMICAL DURABILITY IN SERVICE ENVIRONMENTS

Task 12114

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The objectives of this task are to provide data, measurement methods, and mechanistic understanding of chemically and biologically mediated reactions of materials in their service environments. These processes affect materials durability, the environmental impact of materials processing and use, and the properties and functions of materials such as protective coatings and biocides.

The experimental work of this task focuses on elucidating molecular level interactions of materials with their environments. Biologically mediated processes such as microbial corrosion are included because of the significance of these to materials durability. The nature of the problems addressed has directed development of measurement methods toward techniques for detecting, identifying, and measuring individual chemical species, important as degradation products and transport intermediates, at environmental concentrations down to the ng L<sup>-1</sup> level.

The experimental and theoretical competences, developed in this task to support Division thrusts in materials durability, are broadly applicable to current problems in areas such as environmental quality and emerging aspects of biotechnology. Accordingly, the task responds to requests from NBS Program Offices, other agencies, and the private sector, for measurement data services in these areas uniquely available within the Division. The program of the task thus extends to a broad range of activities as outlined below.

Highlights of major accomplishments for FY82 include:

- Development of measurement methods and preliminary data supporting a new mechanism of anaerobic biocorrosion of bulk iron;
- Incorporation of complementary molecule-specific methods into Mil-Spec development for Navy's major procurement of fleet antifoulant polymers;
- Demonstration of theoretical basis for correlating molecular conformations and shapes with independent measurements by liquid chromatography and nuclear magnetic resonance spectrometry (NMR);



- Characterization of a mercury-reducing enzyme imparting toxic metal-resistance in bacteria crucial to bioleaching technology for copper mining;
- Demonstration of the concentration of organotin biocide residues in marine surface water microlayers as a key component in their environmental fate.

#### Determination of Mechanisms Controlling Biodegradation

Biodegradation processes may be beneficial or detrimental. Anaerobic, biologically mediated corrosion of metals, for example, is now recognized as a multi-billion dollar problem in the United States. Microbial degradation of paints, coatings, building stone, masonry, or concrete are comparable economically significant problems of materials deterioration. On the other hand, microbial metal ore beneficiation processes account for about ten percent of U.S. copper ore production and are increasingly applied to extraction of lean ores of uranium and other strategic metals. Common to these biotransformations is the requirement for measurement techniques that will allow quantitation of metal transport. Study of the controlling mechanisms of degradation, including measurements of rates and key transport metal species involved, can lead to valid assessments of the relative importance of chemical or biological agents. This information is crucial to the choice of timely and effective control or applications strategies.

In FY82 we initiated a new program on anaerobic corrosion of metals, especially iron, with a long-term project recently funded by Office of Naval Research (ONR). A major finding of preliminary work is that the accepted view that anaerobic iron corrosion is caused by sulfate-reducing bacteria acting directly on the metal surface is probably incorrect. Our work indicates that these bacteria rapidly corrode bulk iron under anaerobic conditions by production of highly corrosive metabolic products, and that proximity of the microorganisms to the metal is unnecessary. The corrosive metabolic product is volatile, and may incorporate phosphorus and/or sulfur in its composition, as suggested from element-specific gas chromatography. Our work for ONR will emphasize isolation of this and related gaseous metabolites that can adversely react with metal surfaces remote from the biological source. This work will utilize most of the trace element speciation techniques described in this report, with new applications expected from gas, liquid, and surface characterization methods development.

Beneficial applications of microbial metabolisms affecting stability and transformations of useful materials represents a major output of biotechnology. Many of the measurement methods and resulting data base generated by this task can bear directly on important issues affecting materials science and advanced biotechnology. Of immediate concern are the mechanisms, both genetic and metabolic, that determine metal resistance and fate in microbiological communities. We are actively collaborating with experts in the related fields to augment detailed studies.

The bacterium Thiobacillus ferrooxidans, for example, plays a major role in ore leaching by generating strong oxidizing agents ( $\text{Fe}^{3+}$ ) and by direct oxidation of metal sulfides in situ, yet it is believed that such

widespread activity is sharply inhibited by certain trace metals (Hg, Ag, Mo) occurring in ores. Thus, ppm concentrations of such metals can effectively prevent cost-effective bioleaching of tons of copper in a large leach dump.

We have demonstrated, in collaboration with molecular biologists at Washington University, St. Louis, that T. ferrooxidans can overcome toxic Hg(II) by synthesizing a mercury reductase enzyme that reduces the metal ion to volatile Hg<sup>0</sup>, utilizing NADPH as an electron donor. This is the first demonstration of a mercuric reductase in any autotrophic bacterium and the first demonstration of a mechanism of toxic metal resistance in T. ferrooxidans. Other bacteria, chiefly clinical isolates, produce Hg reductases, but the enzyme from our strain is unique in that it is synthesized constitutively (at all times even if Hg is absent) and differs in its molecular structure from related enzymes recovered from clinical isolates (fig. 1).

Toxic metal processing by T. ferrooxidans is important to the mining industry as well as to the biotechnology field. This generates interest in genetically improving bacteria, including conferring toxic metal resistance, so that more efficient organisms can be developed, capable of bioprocessing or bioaccumulating a wider range of metal ores. We envision as essential future applications of metal speciation to monitor metal ore bioprocessing and to study mechanisms of toxic metal ore recovery. Already, commercial applications of bacteria in metal recovery or cleanup of bioaccumulation of silver in photographic waste effluents are under test by industry. Our successful monitoring of cellular uptake of organotin biocides using both tin-selective liquid chromatography and epifluorescence microscopy, demonstrates how the task may provide underlying measurement methods to support aspects of biotechnology concerned with metals processing.

We interact actively with organizations concerned with reducing avoidable costs from biodegradation, as well as those seeking substitution biotechnology for energy-conserving recovery of low-grade metals from scarce supplies. We participated in the formation of the first international working group of experts on biodeterioration of metals and actively consult with members of the Materials Technology Institute and National Association Corrosion Engineers (NACE) who share our concerns and views on needed future research.

#### Characterization and Performance of Biocidal Organotin Polymers

In FY82, we continued our joint program with the U.S. Naval Ship Research and Development Center (USNSRDC) to develop bases for a Mil-Spec to procure major quantities of tailored organotin polymers (OMPs) for use as fleet marine antifoulants. Under most active development by the Navy are copolymers of methyl methacrylate (MMA) and tributyltin methacrylate (TBTM). Field tests of paints incorporating such OMPs have now passed the four-year mark without failure, and fleet use of 100,000 to 300,000 pounds/year as polymer is planned for 1986.

We are asked to help provide methods for molecular characterization of these polymers which can support a Mil-Spec to insure long-term antifouling



performance. The Mil-Spec will specify molecular characteristics of the OMPs, since field tests are impractical for such a long-lived product and accelerated wear/leaching tests are unreliable while the mechanism of degradation is unknown.

Here, we must combine molecule-specific measurements differing greatly in sensitivity and method to acquire needed information. We have concentrated in two areas which feature the complementary measurement capabilities of tin-specific size exclusion chromatography coupled with graphite furnace atomic absorption detectors (SEC-GFAA) and high field nuclear magnetic resonance spectrometry (FT-NMR), described in last year's report. The first method permits us to quantitatively examine the molecular weight distribution of bioactive organotin groups attached to the polymer chain; the second method permits direct evaluation of local molecular architectures surrounding tin atoms (tacticity) using magnetically active H-1, C-13, and Sn-119 nuclei in samples of these OMPs. C-13 and Sn-119 spectra are proving to be the most informative.

NMR signals of tin and carbon are greatly influenced not only by their local molecular environment, but also by longer range interactions found in large macromolecular arrays such as OMPs. Such distant effects include both composition and stereochemistry (tacticity). Figure 2a shows the proton-decoupled C-13 spectrum of the carbonyl region of OMP-8, a 2:1 MMA-TBTM copolymer. The higher field region arises from carboxyl bonded to C, the other signal from carboxyl bonded to Sn. The fine structure is due to nearest neighbor interactions, and appears to be consistent with the idea that tacticity is nearly random, but with a slight excess of syndiotactic groupings.

Figure 2b depicts the Sn-119 NMR spectrum of the same sample. A comparison spectrum (not shown) of TBTM homopolymer shows absorption peaked at 82 to 83 ppm, and this polymer must have all triads of TBTM-TBTM-TBTM composition. We find virtually no overlap between the Sn spectrum of the homopolymer and OMP-8. This indicates that all triads in the copolymer must contain at least one MMA residue. The "blockiness" of the copolymer is thus proved to be very slight.

The question of molecular weight range optimal for longest effect anti-fouling properties is also of concern. In Annual Reports over the past two years, we have discussed advances in tin-specific SEC-GFAA determinations of Sn content versus molecular weight distributions in candidate Navy OMPs. Representative polymers were shown to contain high (50k Daltons) and low (monomer) tin species, but an absorbed species suspected of being charged has now been detected. By injecting trace amounts (relative to polymer) of weak organic acids at measured intervals following injection of the neutral polymer (fig. 3), the absorbed charged tin-containing species is thereby eluted.

The results have major implications for organotin impurities formed during large-scale commercial production required by the Navy program. We cannot yet state whether the charged species represents a competitive product from the free-radical initiated polymerization of MMA and TBTM or whether this is a degradation product related to the marine fate of the OMP. OMPs stored at -78 °C in tetrahydrofuran for one year tend to



lose part of the tributyltin moiety, possible as a cation, without apparent degradation of the organic backbone. By examining these latest materials isolated by preparatory-scale SEC-GFAA with both C-13 and Sn-119 NMR, we hope to better understand both process and storage deterioration of these valuable materials.

#### Development and Applications of New Speciation Methods

A basic measurement rationale has emerged from this which recognizes and exploits the ubiquitous presence of trace metals and metalloids in virtually all natural and man-made materials. In practical terms, this means that if measurement methods can be devised that assure sufficient selectivity and sensitivity, key elements at certain times, in conjunction with certain materials during some part of their use cycle, will effectively serve as "flags" or diagnostic species for monitoring purposes. To achieve acceptable measurement criteria, development of means for coupling suitable element-specific detectors to sophisticated molecular separation schemes must be pursued.

Last year's report described development and preliminary applications of a new ultratrace method employing a tin-specific flame photometric detector (FPD) automatically coupled to a purge and trap gas chromatograph (P/T-GC). The group is concluding an evaluation of this technique for speciation and quantitation of a heavy metal in a clinical SRM being re-released by the NBS Office of Standard Reference Materials (OSRM) as (new) Freeze-Dried Urine.

In the urine SRMs, volatile sulfur compounds are detected in both S- and Sn-selective modes; involatile ionic tin compounds require borohydride reduction for their volatilization as stannanes into the GC system and are detected only in the Sn mode. Some of the major species identified include  $(\text{CH}_3)_2\text{SnH}_2$  and  $(\text{CH}_3)_2\text{S}_2$ . A monobutyltin species,  $\text{C}_4\text{H}_9\text{Sn}^3$ , (determined as  $\text{C}_4\text{H}_9\text{SnH}_3$ ) appears in the same chromatogram. Quantitative results are summarized in table 1.

Table 1. Concentrations<sup>a</sup> of Tin and Sulfur Species in Previous and New NBS Freeze-Dried Urine SRMs

Species	"Old" SRM	"New" SRM
$(\text{CH}_3)\text{Sn}^{3+}$	1.0	ND <sup>b</sup>
$(\text{CH}_3)_2\text{Sn}^{2+}$	ND	0.46
$\text{C}_4\text{H}_9\text{Sn}^{3+}$	1.5	0.03
Inorganic Sn(II) or Sn(IV)	28.1	ND
$(\text{CH}_3)_2\text{S}_2$	ND	2.73

<sup>a</sup>By method of additions: in  $\mu\text{g/L}$

<sup>b</sup>ND = not detected.

There are both qualitative and quantitative differences between the two SRMs, doubtless reflecting different pooled sources. Detection of a butyltin species in both materials is a notable finding since there are no known biological butylation reactions comparable to biomethylation. These results may indicate human exposure to increased world-wide industrial use of butyltins, at least in the SRM source population. As a wide spectrum of organotins finds greater use in manufacturing and biocides, methods and standards for health monitoring and occupational exposure are needed. The SRM speciation methods now demonstrated can greatly assist in meeting these measurement requirements.

Not only is this work an important use of our methods for the health field, but it provides OSRM with molecular composition of a new SRM in terms of selected elements. Increased requests for information on our work from government, industrial, and academic scientists around the world reflect growing recognition of the importance of, and prospects for, determining trace metal-containing molecular entities in biological materials. This work is the first metal speciation study of a clinical standard, and will greatly assist OSRM in meeting growing needs for related new biological standards.

Another important measurement development for standards involves our continuing use of high performance liquid chromatography (HPLC) coupled with graphite furnace atomic absorption spectrophotometric detectors for element speciation. GFAA depends on thermal processes to remove dissolved organic material from HPLC solvent, to decompose buffers or analyte, and to provide the final atomization step. The ultimate sensitivity or response for different species of the same element can thus vary widely depending on the sample matrix. During the past year, we devised means to improve sensitivity with automated post-column derivatization for HPLC-GFAA, so that little or no modification of the established chromatographic separations would be required. Part of our goal was achieved with a new mixing device that simultaneously receives regulated flows of HPLC effluent and various dilute transition metal salt "enhancer" solutions prior to transport into the GFAA detector. Thereby, the active surface of the GFAA cuvette is continually refreshed with enhancer to yield more reproducible atomizations with sensitivity increases up to 50-fold.

Batch treatments of atomic absorption furnace tubes with many metal salts are sporadically reported to show such enhancements in GFAA. We systematically evaluated a large group of metal salts as GFAA "enhancers" for chromatographic separation procedures required by various on-going sponsored Group projects. HPLC signal improvements for ion exchange (aqueous buffered eluants), size exclusion (organic eluants), and solvophobic (water-alcohol eluants) were tested with classes of metal-containing molecules exhibiting widely different volatility or chemical properties. Effectiveness of any given salt was highly selective, depending mainly on the analyte element. For example, we reexamined samples from prior work for the Navy on speciation of toxic organotins leached by sluicewater during paint removal in shipyards, and achieved greatest enhancement with dichromate ion. The effect, as figure 4 shows, is more pronounced with the volatile tributyltin species (16X), while the less volatile dibutyltin component is much less improved (2X). These results suggest that the mechanism for "fixing" volatile organometallic analytes may



chiefly rely on formation of involatile transition metal adducts or compounds during the GFAA thermal cycle, but additional studies are required to understand potentially different enhancement mechanisms dependent on matrix, selected element, and transition metal. Analogous improvements for a metalloid, arsenic, in complex syncrude oils were obtained with another metal, nickel.

For molecular characterization of arsenic in shale oil by size exclusion chromatography, a huge excess of carbonaceous residue must be charred before GFAA atomization. At the required temperatures over 1000 °C, many arsenic compounds or their decomposition products volatilize and would not be detected. In this case, addition of nickel(II) solutions to the SEC-HPLC system gave optimum signal enhancement for both small, volatile molecules such as dimethylarsenic acid and As-containing macromolecular components of shales. These last results have had great impact on our concurrent collaborative projects dealing with biogeochemical formation of toxic organometals in fossil fuels (Lawrence Berkeley Laboratory) and dearsenation of syncrude shale oils for catalytic upgrading (Mobil Research and Development Corporation).

The long-term commercialization of conventional fuels and chemical feedstocks from domestic reserves of coal and oil shale is dependent upon development of new process technology. We described in last year's report results of our workshop requested by the Department of Energy to assess speciation methodology needed to support efficient processing. The presence of arsenic in oil shale is an example of a substantial processing roadblock to the immediate application of current petroleum refining technology to alternate fossil fuel sources. Arsenic rapidly deactivates costly hydrodenitrification catalysts, necessitating development of measurement methods that will provide a basis for evaluating candidate commercial processes for removal of the element from oils prior to upgrading. Both the molecular forms and quantities of As must be monitored since prospective dearsenation processes rely on both physical and chemical effects which, in turn, are species-dependent.

The reliability and ease of transfer of speciation methodology in this field to the industrial sector will require new standards. OSRM has supported our efforts to evaluate NBS SRM 1580 Shale Oil as a suitable matrix for speciating arsenic. Arsenic concentration in this material (which has been certified only for selected organic compounds) has been determined by GFAA to be  $2 \pm 0.3$  ppm. Using SEC-GFAA procedures noted above, As content of SRM 1580 as a function of molecular weight in the range from 100 to 20,000 was successfully determined. The arsenic eluted at retention volumes corresponding to 1500 to 2000 Daltons as depicted in figure 5. In a novel variation of the chromatographic system, we ran the iron-specific chromatogram simultaneously with the interesting results shown. From these and similar experiments with a wide variety of source shales and oils, characteristic "fingerprints" for the dual As-Fe SEC chromatograms were obtained. This evidence, along with other derivatization experiments, leads to the conclusion that As carriers in process syncrude oils are chemically tied up with iron-containing macromolecules and that earlier, simpler views for removal of As in the form of inorganic ions must be revised.



This difficulty was outlined in a series of papers and talks given during the past year. Our position is that chemical associations between arsenic and macromolecular iron compounds in both naturally-occurring source shale kerogen and the thermally modified retort oils, required a basic study of the underlying chemistry for process monitoring and control. So far we find that lower molecular weight arsenicals are likely bonded to the iron macrocomplexes. Treatment of shale oil with silylating reagents disrupt the As-macromolecular bonds to yield small As-O-Si molecular derivatives speciated by dual As-Si SEC-HPLC. These and related data suggest anionic forms of inorganic and organoarsenicals are dative-bonded to the macromolecules through strong Fe-O-As bonds.

During the past year, Mobil Research and Development Corporation has arranged through our NBS Research Associate Program to join our Group's project on speciation of arsenic in shale syncrudes. Our Associate has verified presence of arsenic acids in shale oil by extraction into aqueous solutions which by ion exchange HPLC-GFAA permit speciation of those inorganic and organoarsenic species expected to require removal for large-scale plant processing. The evaluation of four major industrial dearsenation processes using these methods is underway or nearly completed. The underlying ion-exchange chemistry used by the Group originally to develop the speciation methods and the favored means emerging for oil dearsenation appear closely related. Ultimately, preferred removal techniques may be quantitated for various shale sources on the bases of As MW distributions and associated chemistry. Table 2 provides a summary of preliminary findings for arsenic concentrations in oils from several shales as a function of molecular weight.

Table 2. Relative Abundance (in ppb) of Arsenic in Shale Oils from Various Sources

MW Fraction <sup>a</sup> =	1	2	3	4	5	6
Eastern	38	52	24	19	17	44
Western	186	174	58	29	8	6
Silylated Western	61	177	150	116	17	10
Delayed Coker	6	15	21	11	5	5

<sup>a</sup>1 = > 1600; 2 = 1600-1200; 3 = 1200-800; 4 = 800-400;  
5 = 400-200; 6 = < 200.

Installation of an epifluorescence microscope facility in the Group's laboratories is completed. Initial studies reveal its applicability to a wide range of previously inaccessible materials problems, especially speciation of key metal-containing molecules for in vitro diagnosis of micromorphological changes on surfaces undergoing both biological and chemical attack. The biodeterioration of SRMs, especially those based on naturally-occurring matrices for clinical and environmental users, was rapidly assessed for OSRM using fluorescent dyes to detect metabolites from microbial growth in contaminated liquid (urine) and solid (oyster tissue, orchard leaves). We also applied the technique to directly assay algal and bacterial deterioration of commercial paint films as

part of a new project sponsored by the American Paint Research Institute. Initial results indicate a means for rapidly determining the extent of biological attack in deteriorated paints, and consequently the efficacy of biocide formulations in commercial paints.

Many fluorescing agents, including some that selectively fluoresce with certain metallic ions, are already available, and much future development for their use is expected during coming years. We recently demonstrated the use of 3-hydroxyflavone, which selectively fluoresces with certain organotin ions and Sn(IV), to study the cellular uptake of environmental tin species by bacteria isolated from the Chesapeake Bay. This work has attracted the support of the Office of Naval Research which is assisting us in computerizing our present facility to provide high resolution graphic mapping of surface interactions involved with bacterial corrosion of metallic surfaces. We additionally plan, with other members of the Materials Chemistry Division, to assess the utility of nondestructive testing of ceramics for trace metal distribution patterns by speciation with selective coordination ligands. Such rapid, possibly quantitative optical detection methods can be very cost beneficial for monitoring iron contamination of technological ceramics which may result in catastrophic product failure at high temperatures. The NBS Office of Nondestructive Evaluation is considering a research proposal along these lines submitted at their request.

#### Advances in Separation Science Based on Molecular Topology

This report illustrates the procedure for routine determinations on monitoring for the presence of one or several selected elements within a complex matrix at ultratrace (ppb or ng/g) levels; we can sometimes authenticate their local molecular features by certain independent measurements. The logical prospect fully of exploiting such useful indicators of materials behavior by establishing underlying correlations between molecular architecture and more generally available measurement methods has therefore become a central scientific thrust embodied in much of the Group's output.

Modern HPLC techniques reliably separate a huge variety of molecules by highly selective surface-solution interactions which depend on their size (molecular weight), ionicity (charge), polarity, or hydrophobicity (lipophilicity). Commercially available column substrates provide reproducible, molecularly tailored surfaces and activities that allow rapid equilibration and separation by any one of the above mechanisms. For these reasons, and our preliminary success reported last year, in correlating well-known molecular substituent parameters (QSAR) with chromatographic retention of organometallic compounds, we have sought to extend the basic relationship of molecular shape to chromatography and other key measurement methods.

Currently, our emphasis is placed on computation of total surface areas (TSA) of molecules, derived from literature bond distances, bond angles, and Van der Waals' radii fitted within conformational or stereochemical constraints expected for a molecule situated in a polar medium. Recently, we have been granted access to the PROPHET NET, a very powerful computer system for generating molecular models interactively in any desired



configuration. This advanced computing capability will greatly speed the necessary calculations. Our experimental approach is firmly grounded in solution thermodynamics, and the shape calculations rely upon experimental data independent of solution measurements.

Table 3 illustrates a very simple but important linear relationship found between TSA and water solubility for a series of methylelement molecules, including several well-known to influence global transport of essential and toxic elements.

Table 3. Correlation of Organoelement Geometry with Aqueous Solubility

Compound	TSA, Å <sup>2</sup>	Log Solubility <sup>a</sup>	
		obsd.	calcd. <sup>b</sup>
CH <sub>3</sub> Br	73.1	0.81	0.81
CH <sub>3</sub> I	82.1	1.000	1.149
(CH <sup>3</sup> ) <sub>2</sub> Hg	104.8	1.884	2.018
(CH <sup>3</sup> ) <sub>4</sub> C	120.3	3.126	2.61
(CH <sup>3</sup> ) <sub>3</sub> Sb	128.1	2.9	2.91
(CH <sup>3</sup> ) <sub>4</sub> Sn	153.1	3.637 <sup>c</sup>	3.865

<sup>a</sup>Literature values

<sup>b</sup>r=0.975

<sup>c</sup>unpublished NBS data.

We find further that calculated TSA accurately predicts HPLC retention on columns providing solvophobic separations of neutral organometallic molecules. Additional correlations with other measurements techniques are being evaluated: the linear relationship between TSA and NMR is the most promising because it places a powerful nondestructive spectrometric technique for molecular characterization at high concentrations into a quantitative relationship with the proven ultratrace HPLC-GFAA technique.

Figure 6 summarizes important new relationships for which linear correlations appear general. For a series of organotins similar to those previously discussed, the relationship between Sn-119 FT-NMR chemical shift and  $\pi$  (a biological QSAR established by Hansch) and TSA is compared with a summary of the other correlations noted. Our present line of study examines the most favorable molecular conformation in a given medium and its associated TSA and NMR with respect to "penetration" of diamagnetic solvent molecules to the central magnetically active nucleus, here Sn. The combined effect of the surface area and volume requirements for closest approach between analyte Sn molecule and solvent molecule(s) possibly controls the overall bulk diamagnetic susceptibility term, and chemical shift, of the organotin. In addition to this, parallel NMR



studies evaluating  $^2J_{\text{SnC}}$  and  $^3J_{\text{SnC}}$  spin-coupling constants will be useful in assessing preferred conformations in bulk solution, since these also seem to correlate with  $\log k$  and  $\pi$ .

#### Environmental Measurements of Materials Performance and Fate

The International Tin Research Institute estimates that current world production of all organotins exceeds  $3 \times 10^7$  kg/year. Most of these applications for organotins result in wide dispersal (as paints, plastics, wood preservatives, etc.) in the environment. Unfortunately, relatively little is yet known how these bio-active materials are transported or sequestered in environmental compartments, especially aquatic waters and sediments. In addition to their major fleet antifoulant requirements, the Navy is concerned for environmental impacts of their annual multi-million cubic meter dredging operations which involve sediments receiving increased loadings of organotins as well as other toxic metals. Similar concerns are recognized abroad as well.

Two task activities over the report period bear directly on these concerns. At the request of the Naval Civil Engineering Laboratory, we initiated studies on the nature and rates of organotin leaching from OMP-impregnated wooden pilings for shore installations. These pilings are prepared by in situ polymerization of various organotin-containing precursors directly within the wood matrix, producing a stable, very slow release antifouling preservative. Our project seeks to overcome deficiencies of prior methods for accurate measurements of organotin release rates from such treated materials, i.e., the slow release rates were poorly defined because leachates were at extremely low concentrations and simple total tin measurements yielded little understanding of release mechanisms of active toxicants. Our approach employs combinations of HPLC-GFAA and P/T-GC FPD, described above, to acquire sufficient rate and species data for estimating long-term (years) field effectiveness. Laboratory simulation experiments are designed to complement field measurements.

In considering the environmental transport and fate of organotin biocides used in aquatic systems, our current experience, in agreement with other workers, indicates that very little tin in the form of organotin species exists in bulk seawater. We demonstrated last year that neutral tetramethyltin and some methystannanes occur in polluted harbor waters, but most of the organotins are bound to particulates or sediments. In a recently concluded joint study supported by the Dutch Government (International Agricultural Centre) one of our Group members set up complete speciation facilities in The Netherlands emulating the NBS facilities. Studies of heavily polluted column waters and sediments in Rotterdam's Europort made it clear that relatively little of tributyl- or triphenyltin-based antifoulants in common use there could be detected. Rather, only small concentrations of methyltin species, possibly biogenic, were speciated in sediment pore waters by P/T-GC-FPD. In such harbor waters so heavily laden with petroleum, it is possible that other organotins present would partition into the oil phase preferentially. We intend to continue the joint research with the Dutch, but review of our evidence suggested that we first consider speciation measurements of the aquatic microlayer as an important sink for organotins as well.

The aquatic surface microlayer is a thin (50 to 800  $\mu\text{m}$ ) film at the air-water interface in terrestrial and marine environments. It consists of oleaginous natural and man-made products with natural debris from biological and geological sources. It provides a large array of micronutrients which support very large microbial populations. Over the years, scientists have concluded from total element analyses that considerably amplified concentrations of heavy metals can occur in microlayers in comparison with underlying waters.

As a result of these considerations and our Rotterdam data, we initiated field studies to speciate trace organotins in the surface microlayers of the Chesapeake Bay. Our results to date, though preliminary, are definitive and remarkable. Figure 7 shows that while  $(\text{CH}_3)_2\text{S}$  and  $(\text{CH}_3)_2\text{S}_2$  concentrations in bulk water exceed those in the microlayer, organotins can be concentrated in the microlayer ranging from slight to substantial. Interestingly, chief methyl- and butyltins detected are also those found in the human urine samples. Thus far, we cannot reconcile the relative concentrations of methyl- and butyltin species with expected pollution sources (more butyltins in busy harbors).

These novel results dramatically illustrate the present inadequacy of reasonable data bases for modeling fate of important new industrial toxicants. Since the microlayer is an environment subjected to highest insolation and aerobic conditions, it further seems reasonable that many nonbiological transformations of organotins (and other metal compounds) can occur with possible release of more volatile products into the atmosphere. Investigation of these prospects forms part of our task's long-range objectives.

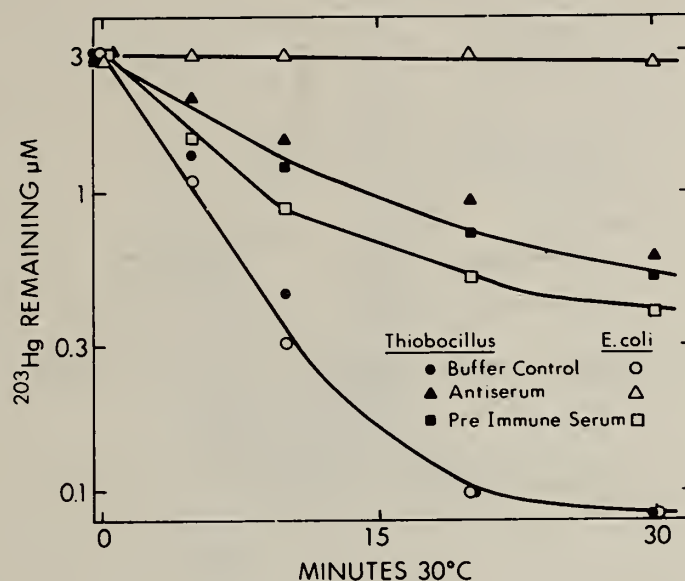
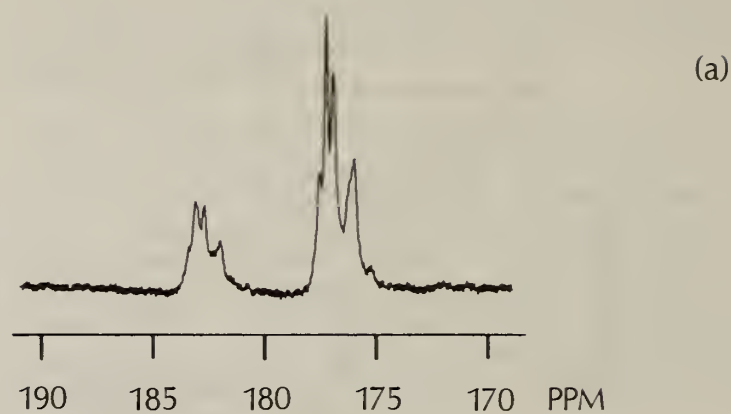


Figure 1 The constitutive mercury-reducing enzyme isolated from *T. ferrooxidans* is molecularly unlike the Hg-reductase produced by *E. coli*. Effects of antiserum prepared against a purified reductase from a clinical isolate, on mercuric reductase from *T. ferrooxidans* (closed symbols) and *E. coli* (open symbols) are shown. The *E. coli* enzyme is totally inactivated by the antiserum ( $\Delta$ ), whereas the *T. ferrooxidans* enzyme is not ( $\Delta$ ). Both enzymes are inhibited nonspecifically by the rabbit serum itself ( $\square$ ,  $\blacksquare$ ).



$^{13}\text{-C}$  NMR of OMP - 2

(Carbonyl region)



$^{119}\text{-Sn}$  NMR of OMP - 2

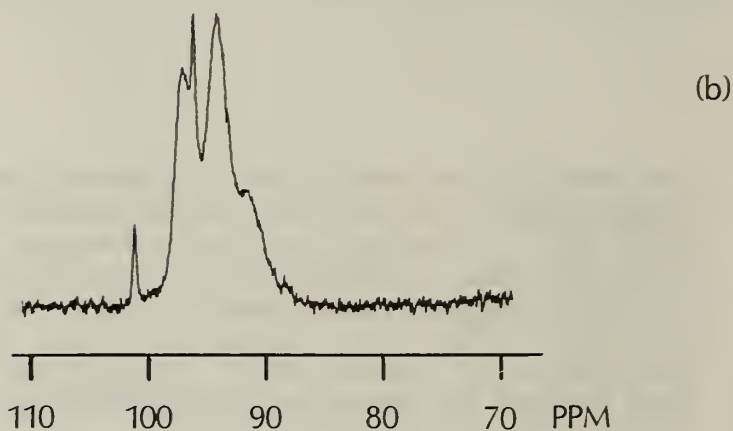


Figure 2 Interpretation of carbon and tin molecular environments in OMP-2 by FT-NMR gives information on polymer tacticity.

- A.  $\text{C-}^{13}$  ( $\text{H-}^1$ ) NMR spectrum (with carbonyl region shown) of OMP-8 in benzene. Spectrometer frequency 50.3 MHz; 1562 scans; 2 level  $\text{H-}^1$  decoupling; total acquisition time 130 min.
- B.  $\text{Sn-}^{119}$  ( $\text{H-}^1$ ) NMR spectrum of OMP-8 in benzene. Spectrometer frequency 74.6 MHz; 400 scans; nuclear Overhauser effect suppressed; total acquisition time 33 min.

# OMP - 2

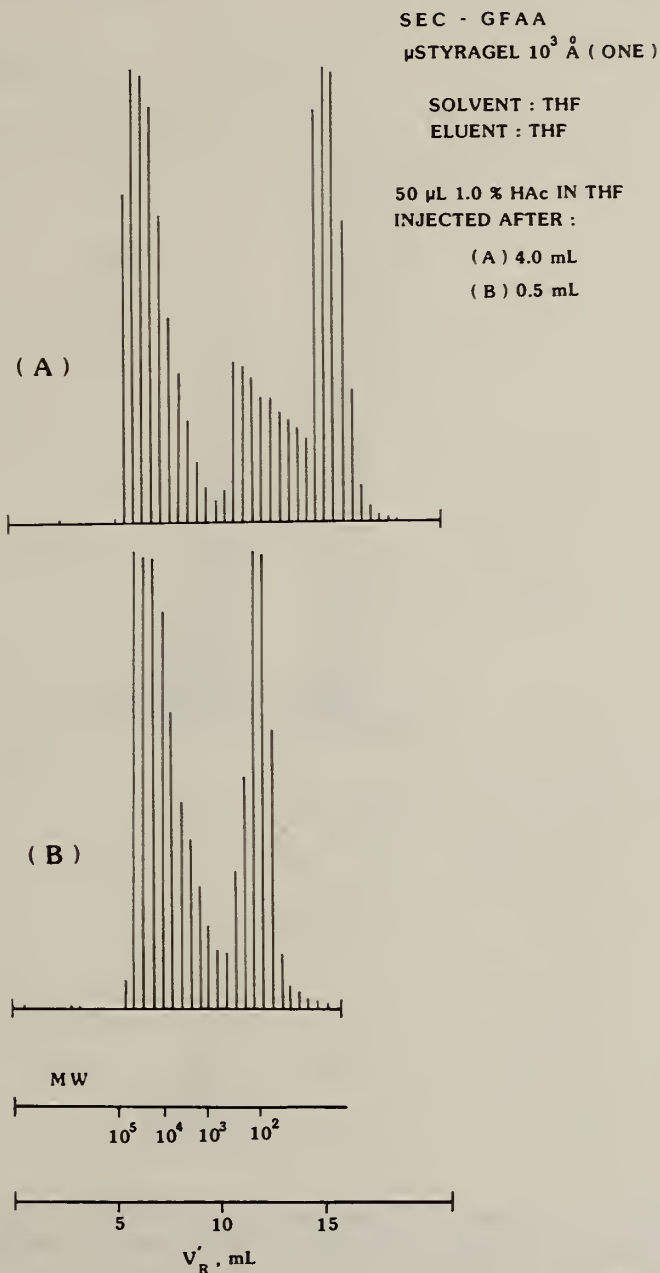


Figure 3 Tin-specific SEC-GFAA chromatograms of OMP-2 (a copolymer) illustrate desorption by injecting acetic acid into THF mobile phase. Abrupt termination of tailing behavior is due to reduced retention of absorbed charged species, possibly tributyltin cation.

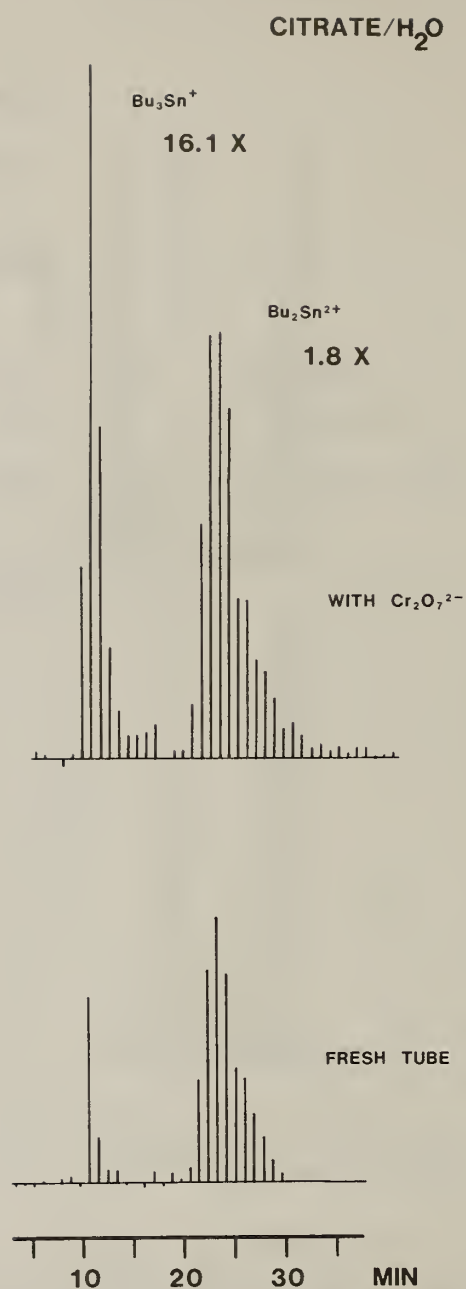


Figure 4 Tin-specific HPLC-GFAA chromatograms are compared for a leachate solution from shipyard grits resulting from spent antifouling paint removal. The lower chromatogram shows GFAA response without co-mixing dichromate solution in the transfer cup; the top chromatogram illustrates typical results with additions of Cr enhancer.



NBS SHALE OIL SRM 1580

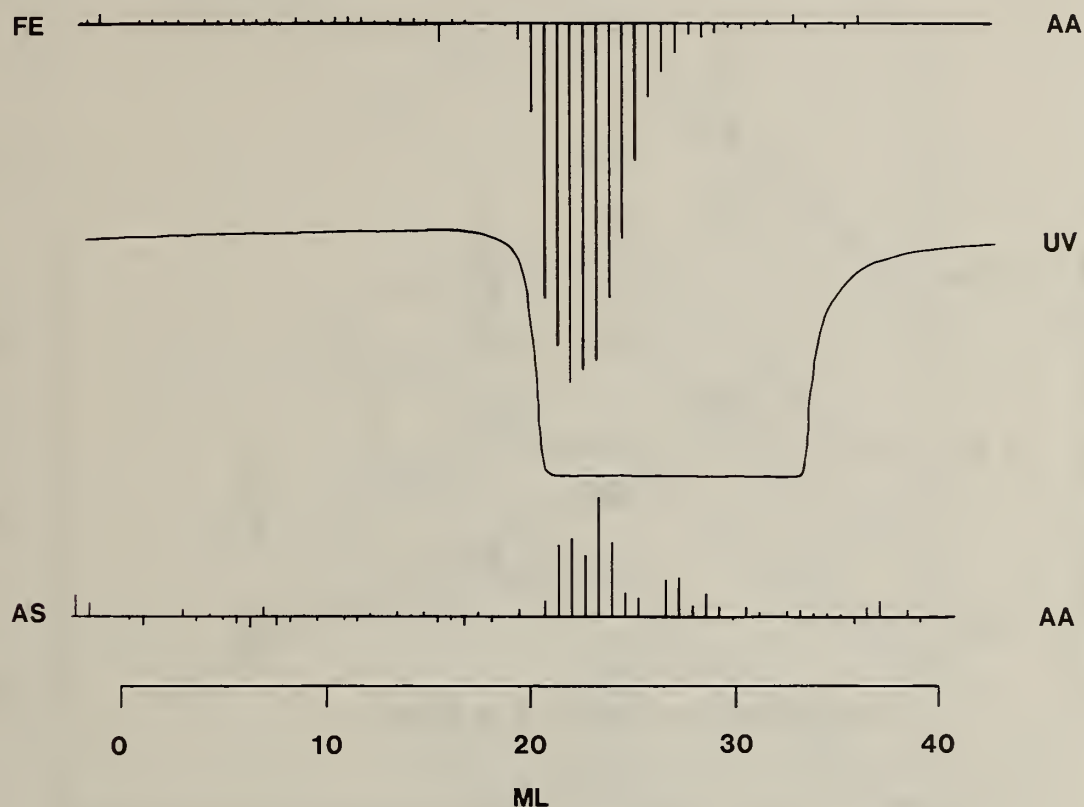


Figure 5 Dual-element SEC-GFAA chromatograms specific for As and Fe are compared for the NBS Shale Oil SRM in tetrahydrofuran. The maximum absorptivity in the tandem UV trace indicates the heavy organic loading of the oil. Coelution of As with Fe at 22 mL suggests common macromolecular carriers with molecular weights of ca. 2500. Post-column addition of Ni(II) enhanced the As signal and insured equivalent As response throughout the elution.

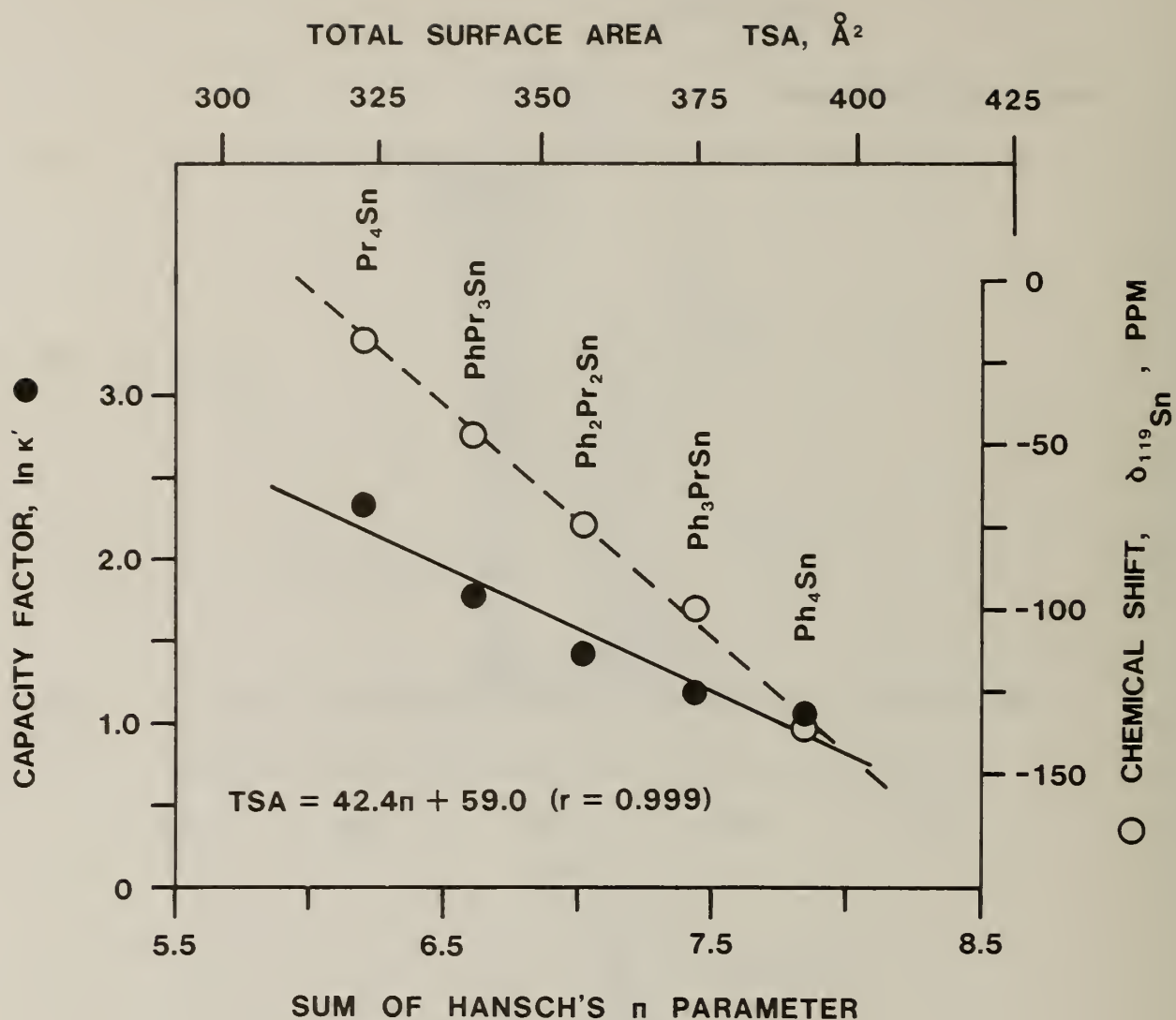


Figure 6 Log of column capacity factor,  $\ln k'$ , (left) and Sn-119 NMR chemical shift,  $\delta$ , (right) plotted against total surface area, TSA, (top) for a series of molecules,  $(n\text{-C}_3\text{H}_7)_n\text{Sn}(\text{C}_6\text{H}_5)_{4-n}$ . TSA is directly proportional to the sum of Hansch's  $\pi$  parameter for individual substituents (bottom). Curvature in the Hansch -  $\ln k'$  correlation is thought to derive from lack of correction for preferred molecular conformations in the simple additivity rules used.

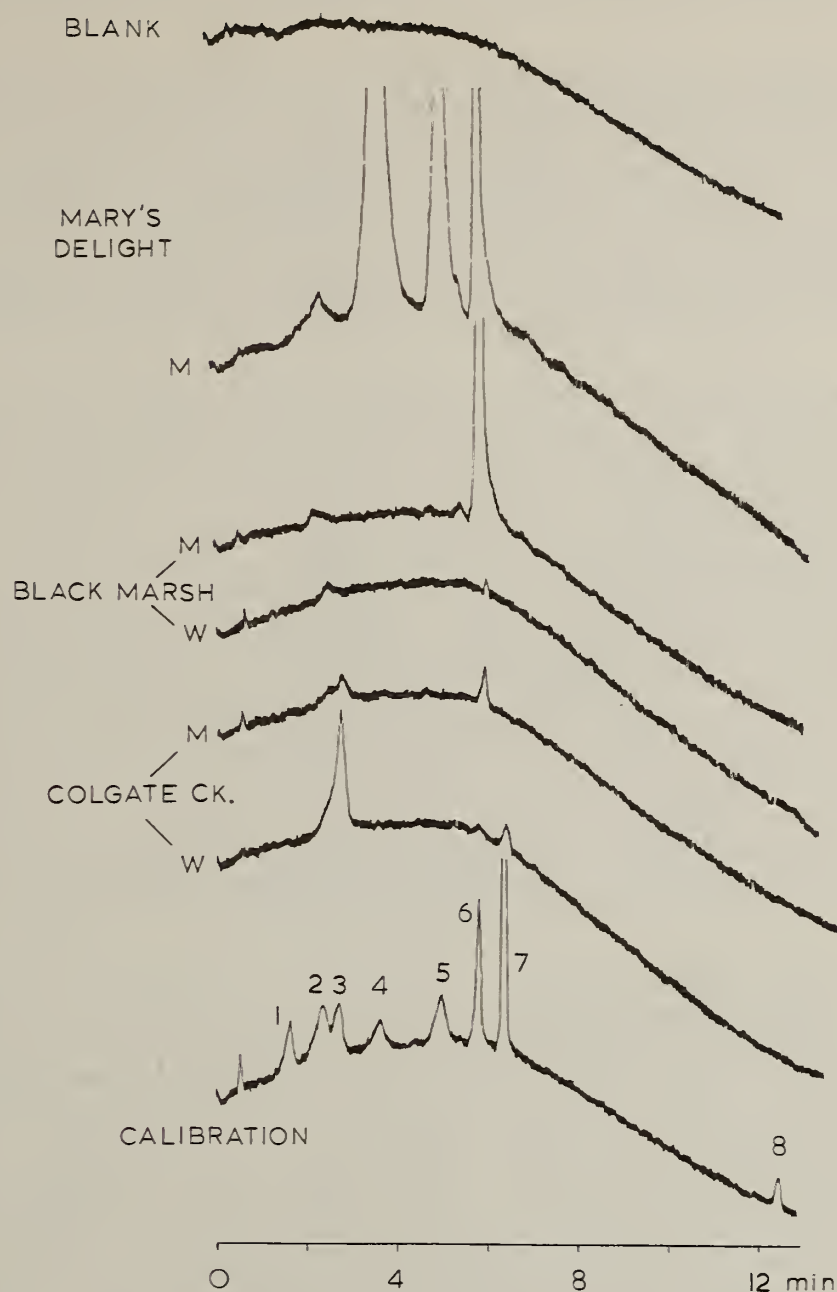


Figure 7 P/T-GC FPD detection of organo-tin and -sulfur compounds from surface microlayer (M) and underlying surface water (W) are compared for various stations in the Chesapeake Bay. The blank (top) represents a typical water rinse of the clean teflon sampler sheet (1.6 m<sup>2</sup>). Authentic compounds in the calibration mixture were: (1) CH<sub>3</sub>SnH<sub>3</sub>; (2) (CH<sub>3</sub>)<sub>2</sub>SnH<sub>2</sub>; (3) (CH<sub>3</sub>)<sub>2</sub>S; (4) (CH<sub>3</sub>)<sub>3</sub>SnH; (5) (CH<sub>3</sub>)<sub>4</sub>Sn; (6) C<sub>4</sub>H<sub>9</sub>SnH<sub>3</sub>; (7) (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub>; (8) (C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>SnH<sub>2</sub> with samples treated by borohydride.





## HIGH TEMPERATURE MATERIALS CHEMISTRY FOR PROCESSING AND DURABILITY

### Task 12115

The principal task objective is to provide a general high temperature chemistry measurement science base for advanced/substitute/conventional materials processing (e.g., ceramics and glass) and service behavior (e.g., hot corrosion and slagging). This objective is accomplished through advancement of experimental methodology, modeling of ceramic/metal gas-liquid-solid equilibria, and through evaluation-compilation and dissemination of, Phase Diagrams for Ceramists, books which emphasize systems containing oxides, sulfides, sulfates, halides, C- and N-containing compounds, and involve solid, liquid, and gaseous species.

Molecular specific experimental methodologies and theoretical modeling tools are being developed and applied to the determination of basic thermochemical and kinetic data and chemical mechanisms for interactions of metals, ceramics, and glasses with aggressive gaseous high temperature service environments. These methods primarily emphasize the identification of molecular species, together with accurate measurement and model predictions of their concentration, spatial, and temporal distribution in high temperature vapors and gases, and in the presence of complex solid or liquid phases. The related in situ measurement problems of temperature and flow (gas phase) are also addressed by this task. Characterization of condensed phase composition and structure is achieved by x-ray and neutron diffraction, electron microscopy, and electron spectroscopy for chemical analysis (ESCA). We have separated the principal task into four subtasks: (1) Chemical Vapor Transport in Reactive Atmospheres; (2) Phase Diagrams for Ceramists; (3) Characterization of High Temperature Gaseous Service Environments; and (4) Synthesis, Structure, and Dielectric Properties of Complex Oxides.

The results of this work are required for (a) performance predictions and test method development in new high technology applications such as coal-combustion and conversion and advanced propulsion systems, and (b) to support materials processing at high temperatures including chemical vapor deposited coatings, and metallurgical, ceramic, and glass processing. In addition to base program support, the task addresses other NBS program and other agency needs, including those of the Office of Standard Reference Data (OSRD) (phase diagram evaluation/compilation), DOE-Fossil Energy (alkali vapor transport), Army Research Office (ARO) (alkali chemistry in flames), NASA (gravity effects on flames, levitation calorimetry of liquid tungsten), Dupont-DOE Savannah River (vaporization of nuclear waste glass). An expanded effort in the Phase Diagrams for Ceramists (PDFC) activity is expected in FY83 with probable new support from the American Ceramic Society.

Major accomplishments during FY82 include the following:

(1) Volume IV of Phase Diagrams for Ceramists, containing 570 critically evaluated new diagrams of metal-oxygen, metal-oxide, and oxygen-containing radical type systems, was published by the American Ceramic Society. Final editing of Volume V, containing about 750 new diagrams of halide, sulfide, oxynitride, aqueous, and ceramic-gas systems was substantially completed.

(2) A new theory for mixing of complex liquid and solid phases has been developed and validated (by comparison with experimental activity and phase equilibria data) for representative ceramic, slag, glass, and molten salt systems containing  $K_2O$ ,  $CaO$ ,  $Al_2O_3$ , and  $SiO_2$ ; or  $PbCl_2$ ,  $CsCl$ ,  $PbBr_2$ ,  $NaBr$ ,  $KBr$ , and  $CdCl_2$  in the latter case.

(3) Reactions between  $HCl$ -containing gases and glass or dolomite substrates, leading to alkali vapor transport have been shown to be highly rate limited. This indicates that chemical kinetic factors must be included in current thermodynamic modeling efforts for the prediction of alkali vapor transport in coal conversion/combustion systems.

(4) The effect of particle size on sintering properties (density and strength) of potassium and calcium aluminosilicate phases has been determined, leading to a new synthesis of refractory ceramics with improved density and strength.

(5) Further refinement of the structural characteristics of lithium insertion type phases is being carried out in a collaborative study with J. Cava, Bell Laboratories, using the unique capabilities of the NBS materials research reactor. These materials have significant potential in a wide variety of new engineering applications because of their fast ion conduction properties. For example, Bell Laboratories, has recently applied for a patent on an innovative high energy battery utilizing the special characteristics of Li-insertion phases as electrolytes.

(6) The "continuous" phase transition in  $ZrTiO_4$ , an important microwave dielectric, was characterized and single crystals containing no superstructure, and both incommensurate and commensurate superstructures were prepared by various techniques. The influence of  $SnO_2$  on the unique characteristics of this phase transition were elucidated.

#### Chemical Vapor Transport in Reactive Atmospheres Subtask 1 of Task 12115

J. W. Hastie, D. W. Bonnell, E. R. Plante, A. B. Sessoms, and W. S. Horton<sup>1</sup>

<sup>1</sup>Consultant

This subtask develops and applies new or improved measurement techniques to the molecular-level analysis of vaporization processes for high temperature solids (e.g., ceramics) and melts (e.g., coal slags, glasses, and salts) in process atmospheres containing reducing, oxidizing, carbonated, halogenated, sulfated, and hydrous components. These conditions and the data obtained are generic to high temperature process environments, and particularly those where hot corrosion and high temperature oxidation are materials-limiting factors. For example, in the developing technology of pressurized fluidized bed combustion (PFBC), removal of coal and dolomite-derived alkali (Na and K-containing species) impurities to a gas stream concentration level below 0.02 ppm is necessary to control hot corrosion of turbine blades in PFBC. Our participation, at DOE's request, in the DOE-Morgantown Energy Technology Center R&D program on particulate and alkali control in coal combustion process streams, provides for close interaction and technology transfer with Industrial

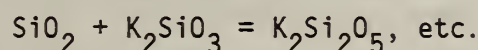
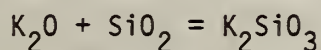


participants, particularly General Electric, Westinghouse, the Electric Power Research Institute, Exxon, and a number of relatively small air pollution technology companies. Our expertise in this area has also led to a very recent request, and a formal collaborative program, by the DuPont Atomic Energy Division for NBS to carry out vapor transport measurements over simulated nuclear waste glass materials. These data are urgently required for the design of process conditions in isolating nuclear wastes in glass materials.

In cooperative work with DOE sponsors, the recent measurement focus has been on ceramic, coal slag, and glass systems in atmospheres typical of coal gasifiers (CG), and pressurized fluidized bed combustors. These extreme conditions have required continued development of the transpiration (TMS) and modulated molecular beam Knudsen effusion (KMS) mass spectrometric techniques. Complementary efforts in data-base (solution activities, species Gibbs energies,...) acquisition and computer modeling have also become an integral part of this extreme-environment characterization effort during the past year. For most of the coal conversion and combustion systems of interest, the chemical state of Na- and K-containing species represents a pervasive theme in our understanding of the high temperature processes and of materials durability problems (e.g., in CG and PFBC). Examples of recent experimental and modeling activities pertinent to these problems are summarized below.

#### Computer Modeling

The large body of vapor pressure and related thermodynamic activity data obtained in our laboratory in recent years has provided us with a unique opportunity for data systematization and testing of various predictive models. During the past year we have developed a highly successful computer-based model for the prediction of solution activities, vapor pressures, and (potentially) phase equilibria in ceramic, coal slag, glass, and molten salt systems. The basis of this model, is the assumption that condensed phase activities, or effective concentrations, are determined primarily by multicomponent equilibria between complex liquid/solid components. Thus, for example, the activity, or effective concentration, of  $K_2O$  in  $K_2O-SiO_2$  mixtures is determined by competing equilibria (solids/liquids) of the type:



Once equilibrium between these component liquids/solids is established the mixture is considered to be ideal with respect to all of the postulated components. This approach contrasts with classical solution theory where only  $K_2O$  and  $SiO_2$ , for example, would be considered as solution components in a thermodynamic description.

A comparison of model predictions and experimental data for K-vapour pressures over  $K_2O-SiO_2$  mixtures is given in figure 1. Note that the two sets of data in best agreement are represented by our experimental and model results. The model has also been successfully applied to glass systems and typical results are given in figure 2 for the SRM-621 glass. Note

the excellent agreement between our Knudsen effusion mass spectrometric data (Plante curve) and model points. Table 1 indicates the glass overall composition together with the component liquids and solids considered in the model calculations.

Table 1. Model Components in SRM-621 Glass.

Wt. % = Na<sub>2</sub>O (12.71), K<sub>2</sub>O (2.01), CaO (10.71), MgO (0.27), SiO<sub>2</sub> (74.3), Al<sub>2</sub>O<sub>3</sub> (2.77)

Significant components (liquid) at 1400 K<sup>a</sup>

Na <sub>2</sub> SiO <sub>5</sub>	K <sub>2</sub> Si <sub>4</sub> O <sub>9</sub>	SiO <sub>2</sub> , CaSiO <sub>3</sub>
Na <sub>2</sub> SiO <sub>3</sub>	K <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	CaO·MgO·2SiO <sub>2</sub>
	K <sub>2</sub> SiO <sub>3</sub>	(Al <sub>2</sub> O <sub>3</sub> ·CaO·4SiO <sub>2</sub> )

Insignificant (liquid + solid)<sup>b</sup>

Al <sub>2</sub> O <sub>3</sub>	3Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>
K <sub>2</sub> O	K <sub>2</sub> O·9Al <sub>2</sub> O <sub>3</sub>
Na <sub>2</sub> O	CaO·Al <sub>2</sub> O <sub>3</sub>
CaO	2CaO·MgO·2SiO <sub>2</sub>
MgO	Al <sub>2</sub> O <sub>3</sub> ·CaO·2SiO <sub>2</sub>
KAlO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> ·2CaO·SiO <sub>2</sub>
KAlSiO <sub>4</sub>	12CaO·7Al <sub>2</sub> O <sub>3</sub>
KAlSi <sub>2</sub> O <sub>6</sub>	

<sup>a</sup>Significant components are those having > 10<sup>-4</sup> mole fraction concentration as predicted by the computer model.

<sup>b</sup>Insignificant components are those considered but calculated to be present at < 10<sup>-4</sup> mole fraction.

Based on initial external responses to our model we expect broad future usage by industrial and other research and development communities. In recent months the following establishments have expressed an interest in utilizing our computer program, data base, and related material: DOE-Morgantown (slag modeling); DuPont-Wilmington (glass-metal wetting); A. Cooper-Case Western Reserve (diffusion in glass); DuPont-Savannah River (nuclear waste processing); PPG-Pittsburgh (fluoride glass volatility in fiber production); CSIRO-Sydney (fluidized bed coal-slagging);



New South Wales Electricity Comm.-Australia (steam plant design for high slagging coals); and St. Gobain-France (glass processing). Also, Dr. N. Christensen of F. L. Smith and Company (Denmark) has recently pointed out to us the potential importance of this modeling activity to alkali vapor transport in cement processing.

In principle the model should also permit calculation of phase diagrams and we will pursue this aspect in future work. We should stress, however, that the viability and reliability of this model require continued testing as additional components are added to the database. Thus this closely coupled experimental and modeling effort will be continued in FY83 for optimum development and public dissemination of this model.

#### Alkali Vapor Transport Over Complex Oxide, Slag, and Glass Systems

Dolomitic limestone is used for sulfur retention in fluidized bed combustors. However alkali impurities in the limestone, together with the neutralizing effect of this basic material on alkali-containing coal mineral impurities (e.g., illite), can lead to excessive alkali vapor transport and corrosion of downstream components. To determine whether alkali vaporization from dolomite itself will exceed the tolerance (to hot corrosion) limits for turbine gas streams we have obtained vapor pressure data, as shown in figure 3. The good agreement between the TMS and KMS data is noteworthy. The several order of magnitude difference in characteristic residence times for these two techniques suggests that the system readily achieves thermodynamic equilibrium. Note that at the 1200 K temperature expected of PFBC operation the alkali pressure is above the turbine tolerance limit of 0.02 ppm.

Alkali absorbant materials such as glass, slag, bauxite, etc., are under study by various industrial laboratories (G.E., Westinghouse) associated with PFBC development. High alkali vapor pressures over these materials may limit their efficiency as absorbants. Also, alkali sensors are under development for monitoring combustion gas streams and reference vapor pressure data are desirable at the temperatures and partial pressures of usage. In response to these needs for accurate alkali partial pressure data over glass systems, we have obtained data over the SRM-621 glass as shown in figure 2. These data were obtained by the KMS method after vacuum outgassing. The complementary TMS experiments showed anomalously high Na pressures due to the presence of unreacted carbonate impurity. Thus, this SRM-621 glass is not suitable for vapor pressure studies without prior purification.

#### Alkali Vapor Transport in HCl Atmospheres

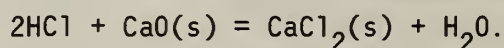
Under service conditions, atmospheric components such as  $H_2O$ ,  $HCl$ , and  $O_2$  can be expected to significantly modify alkali vapor transport through mass action effects or the formation of new molecular species. In coal conversion and combustion processes  $HCl$  is an important gaseous impurity, particularly in its anticipated reactivity with alkalis to yield volatile species such as  $NaCl$ ,  $KCl$ , and  $CaCl_2$ . New experimental work has been initiated on heterogeneous systems containing glass and dolomite together with  $HCl$  gas using the TMS and KMS techniques. Sufficient data have now been obtained to reveal a number of potentially important novel aspects



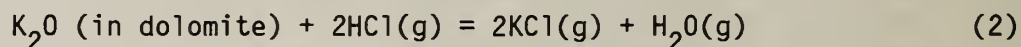
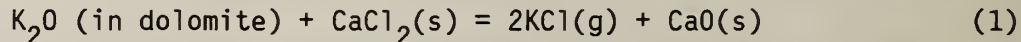
of these heterogeneous processes. First, even though the high temperatures involved (1000 to 2000 K) and the relatively long gas residence time (up to 20 s) would normally ensure attainment of thermodynamic equilibrium, instances of nonequilibrium behavior were found.

Typical data for the SRM-621 glass, HCl system are shown in figure 4. Note that the production of NaCl is many orders of magnitude less than the equilibrium value. In spite of this lack of equilibrium, transport of alkali as NaCl is much more important than vaporization as Na. At relatively low HCl pressures, the deviation of  $K_p$  from the steady state value is most likely due to an error in the HCl pressure measurement because of scattering of residual HCl into the ion source. At relatively high HCl pressures ( $> 10^{-6}$  atm) a steady state is no longer achieved. Presumably, at high vaporization-rate conditions, the rate of diffusion of Na through the glass becomes rate limiting.

Analogous studies were made for the dolomite SRM 88a-HCl system using the KMS and TMS techniques. At relatively low temperatures of 400 to 800 °C, using the TMS technique, large amounts of HCl were consumed with a concomitant production of H<sub>2</sub>O. Also, similar KMS experiments showed CaCl<sub>2</sub>(g) at pressures close to those for unit activity CaCl<sub>2</sub>(s). These observations are indicative of the initial process



Alkali vapor transport from dolomite in the presence of HCl gas can be expressed by the processes:



Since the activity of K<sub>2</sub>O in dolomite is known from our mass spectrometric measurements in the absence of HCl, and the Gibbs energies of formation are known for all the reaction components, the thermodynamic equilibrium constants can be computed for reactions (1) and (2). The apparent equilibrium constants (KMS experiments) determined from the observed pressures of KCl, H<sub>2</sub>O, and HCl are about a factor of 10<sup>14</sup> less than the true equilibrium values. It is somewhat surprising that both of these reactions showed a similar large degree of departure from equilibrium. We had expected reaction (1) to be more favorable based on our previous experience with solid-solid alkali exchange processes. Analogous TMS experiments indicated only a factor of 10<sup>8</sup> departure from the equilibrium values for both KCl and NaCl vapor transport. The higher efficiency of TMS as compared with KMS experiments can be attributed to the longer gas residence times and higher HCl pressures used with the TMS method. As was the case with the glass-HCl system, even though the reaction to produce alkali halide is kinetically hindered, a significant enhancement in alkali vapor transport results from the presence of HCl gas. Further work on the extent and reaction rates of these gas--solid (or liquid) reactions will be carried out in FY83.

Phase Diagrams for Ceramists  
Subtask 2 of Task 12115

L. P. Cook, R. S. Roth, T. Negas, M. A. Clevinger, D. McKenna, and  
L. Frankenburger

This subtask responds to an established NBS role in the critical evaluation, compilation, and dissemination of phase diagrams for use by ceramists. As a joint NBS-ACerS activity (with some OSRDS support) the work is closely coupled with current needs as perceived by NBS and the ACerS advisory committee. R. S. Roth, T. Negas, and L. P. Cook currently serve as General Editors of the volume, and commentaries are prepared by 31 individuals, representing an international team of contributing editors. The NBS editors are responsible for the accuracy of the final product evaluated diagrams and this requires expert working knowledge of the experimental and, to an increasing extent, theoretical aspects of phase diagram construction.

Efforts are in progress to provide computer control over the bibliography and for phase diagram manipulation and editing. In the past year the book manuscript text has been converted to magnetic storage and transmitted in this format to the ACerS publisher, thereby eliminating type setting errors and additional proofreading. Efforts to computerize the construction of phase diagrams have also been implemented during the past year. Similarly a significant effort has gone into developing theoretical approaches to the a priori calculation of phase diagrams for ceramic systems, e.g., see Subtask 1.

A major accomplishment during FY82 was the publication of Volume IV, Phase Diagrams for Ceramists, by the American Ceramic Society. This latest volume of the series contains 590 new phase diagrams with commentaries describing experimental methods, accuracy and precision of data, and comparison with other work. Phase diagrams of metal-oxygen and metal-oxide systems and systems with oxygen-containing radicals are included in this volume. Volume V in the series, scheduled for publication in FY83, will contain 750 new diagrams of halides, halides with other substances (especially metals and oxides), sulfides, oxycarbides and oxynitrides, aqueous systems, systems with CO<sub>2</sub>, and ceramic-gas (primarily C-O-H) systems. Final editing of Volume V will be completed in FY82 and the manuscript will be submitted to the American Ceramic Society for publication.

Preparation of Volumes VI and VII in the series also continued during FY82. Approximately 500 additional references for evaluation were mailed off to contributing editors, and many commentaries have already been received. These volumes are scheduled for publication by 1985.

It has been long recognized that the use of computerized methods is essential for operation of the Phase Diagrams for Ceramists Data Center. During FY82 a proposal was submitted to the American Ceramic Society--the theme was extensive use of computerized data base management methods with concomitantly increased support to contributing editors. This proposal was enthusiastically received by the Society, and was passed by its Executive Committee. Two committees were then appointed: (1) an Ad Hoc Advisory Committee on Phase Equilibria Data Center, chaired by



L. P. Cook, which was given its official mission by incoming Society president R. J. Beals at the American Ceramic Society Annual Meeting in Cincinnati, in May; (2) a Fund Raising Committee chaired by former president J. I. Mueller, with S. J. Schneider of NBS as one of its members. The former Committee, as well, consists of a number of respected people in the ceramic science community: T. B. Lindemer, Oak Ridge National Laboratory; K. E. Spear, Penn State; A. Muan, Penn State; D. E. Day, Univ. Missouri; E. Ruh, Carnegie-Mellon; A. M. Alper, GTE; B. H. Baker, ARMCO; J. J. Brown, Virginia Tech.; P. K. Gallagher, Bell; N. N. Ault, Norton; A. H. Heuer, Case Western Reserve; B. Schwartz, IBM; R. A. Eppler, PEMCO; and G. H. Beall, Corning. The first meeting of this Committee was held in May. One of the outcomes was a consensus that the Data Center should expand coverage of nitride and oxynitride ceramics. To discuss further this and other future directions, in particular the use of computerized methods in phase diagram manipulation, a second meeting will probably be scheduled in the near future. It is anticipated that the work of this Committee ultimately will be of use to the Fund Raising Committee.

In-house efforts aimed at initial implementation of some of the actions mentioned in the comprehensive proposal discussed above, pending American Ceramic Society action, were begun during the fiscal year, largely through the auspices of the Office of Standard Reference Data. Assistance to the Data Center has been of two forms: (1) programming assistance, and (2) a very recent grant of DOE funds. A professional programmer (C. Messina) has made progress in developing software for development and management of the computerized bibliographic file which is essential for operations such as indexing, searching, sorting, and updating. It is expected that entry of bibliographic information using this system can begin in the near future. A current concern is the prospect of extensive use of computer graphics for phase diagram manipulation. Because of the volume of materials to be handled it is desirable to determine the most efficient and yet accurate method of storage and recall of phase diagram information. A feasibility study of this is being undertaken by in-house personnel (primarily P. K. Schenck). Ultimately a modeling input will be required for the production of phase diagrams and efforts to gain familiarity with available software are continuing. To this end L. P. Cook attended a seminar on the FACT system for calculation of phase equilibria at McGill University in May, and it is anticipated that substantial use of this system will be made in the near future. Contacts with other researchers doing calculations of phase equilibria at the recent CALPHAD meeting at Argonne in May have also proved useful, especially interactions with L. Lukas, B. Sundmann, R. Howald, P. Spencer, and A. Pelton.

#### Characterization of High Temperature Gaseous Service Environments Subtask 3 of Task 12115

P. K. Schenck and J. W. Hastie

Objectives of this subtask are to develop and optimize measurement techniques for characterizing high temperature gaseous environments, including flames, and to apply the methodology to assessing and predicting the performance of materials in those environments. During



FY82, further refinements have been made to several new combustion diagnostic techniques for further application to mechanistic studies of combustion modification, including flame and smoke retardance. These techniques rely on laser excitation of electronic states in atoms and molecules. We have also utilized the enhanced thermal ionization of laser excited atoms (the optogalvanic effect or laser enhanced ionization) to modify the neutral/ion ratio from which species flow velocity and diffusion parameters can be determined.

In collaboration with the Center for Analytical Chemistry, modeling and experimental studies have continued on the collection mechanism of ions and electrons from laser enhanced ionization (LEI). Maximum sensitivity is obtained when a water cooled probe is inserted in the flame to collect the signal produced by electrons and ions formed by LEI using pulsed lasers. Near unity collection efficiency is possible if the laser beam producing the electrons and ions is within the sheath formed by the background flame ions around the probe (held at a negative potential with respect to the burner body). The reason for this has been verified in computer modeling of the motion of the LEI formed ions and electrons in the flame. The cathode sheath is the region of highest electric field and the electrons and ions move fastest in this region. The computer modeling consists of an animation which demonstrates that the electrons are rapidly repelled to the edge of the sheath due to their high mobility compared to the ions. This results in a current in the flame and an induced charge on the anode (burner). On a time scale about 200x slower the ions move toward the cathode where they are collected contributing to the signal. Further modeling and experiments are planned to study the possibility of charge transfer to species with higher mobility to enhance the ion component of the signal as well as the role of ambipolar diffusion in the case of CW laser LEI.

Also in collaboration with the Center for Analytical Chemistry, work continues on the study of the neutral atom depletion by LEI and its application as a combustion probe. It is possible via LEI to locally ionize more than half of the neutral metal atoms (typically Na) in the flame. This local depletion persists because the ternary recombination process is slow. A second laser beam is used to map out the motion of the local neutral atom depletion in time and space. A flame velocimeter with spatial resolution of 1 mm and velocity accuracy better than 3 percent was demonstrated for laminar flow flames. Current work on this probe is directed at refining the measurement of diffusion coefficients of neutral atoms in flames.

A krypton ion pumped near-IR dye laser has been installed for studies of K in flames. Similar concentration mapping with and without LEI "holes" should be possible in normal as well as inhibited K seeded flames. This work will be done in support of Army and NASA contracts on Secondary Flash Suppression and Gravity Effects in Flames respectively. The IR dye laser will allow us to monitor K concentration either by absorption or LEI (to the ppb level). Temperature measurements will be made by computer controlled Raman spectral experiments. The effect of temperature on the Raman spectra is shown in figure 5. These Raman spectra were calculated on our laboratory automation computer which will control the monochromator and data acquisition for automatic temperature profiling of normal and

inhibited flames. During FY83 we plan to couple these laser-based flame diagnostic techniques with the high pressure sampling mass spectrometric apparatus for simultaneous measurements of temperature and species concentrations.

Figure 5 also demonstrates the current capability of our automation equipment for generating camera-ready figures for publication. During the last year the Hershey character set used on the NBS Central Computer was transferred via the NBS Net to our local laboratory automation computer. A demonstration program using these characters has been given to over 20 users including NASA, COMSAT, NOAA, and the Coast Guard. Plans are currently underway to issue a flexible disc with the user defined characters in conjunction with an NBS Report through the Office of Standard Reference Materials. This would make the data file available to over 50 thousand HP digital plotters at a modest cost. The implementation of the high quality computer calligraphy should also speed up the automation of the preparation and editing of Phase Diagrams for Ceramists under Subtask 6.

#### Synthesis, Structure, and Dielectric Properties of Complex Oxides Subtask 4 of Task 12115

R. S. Roth, L. P. Cook, J. L. Waring, A. E. McHale, H. S. Parker<sup>1</sup>,  
R. J. Cava<sup>2</sup>, and L. P. Domingues<sup>3</sup>

<sup>1</sup>Research Associate, American Ceramic Society

<sup>2</sup>Guest Worker from Bell Telephone Laboratories

<sup>3</sup>Guest Worker from Trans-Tech, Inc.

This subtask addresses structure-property relationships for oxides important as refractory or electronic ceramic materials. It also couples closely with the nonexperimental subtask on Phase Diagrams for Ceramists and provides phase equilibria data on key systems not covered satisfactorily in the Phase Diagram compilations.

#### Sintering in the $K_2O-Al_2O_3-SiO_2$ System

Potassium aluminosilicate and related materials appeared to offer particular promise, from a chemical standpoint, as refractories resistant to high temperature alkali corrosion. We have investigated the role of sintering in preparation of these ceramics with improved density and strength. Sintering phenomena are closely related to and governed by classical phase equilibria, with the added complexity of localized interfacial phase equilibria in which surface energies play an important role.

Although potassium aluminosilicates sinter, they do not densify appreciably during thermal sintering, if micron-sized powders are employed. Classical sintering theory predicts that either volume diffusion or grain boundary diffusion must be increased if densification is to be achieved. Volume diffusion can be increased through the use of reactive sintering if appropriate reaction paths are available. The only satisfactory route found to date has involved use of  $KAlSi_3O_8$  glass and  $KAlO_2$  to produce  $KAlSi_2O_6$  ( $KAlSiO_4$  produced by this method is not dense). The



apparent reason for relative success of this method is the high viscosity of the  $\text{KAlSi}_3\text{O}_8$  glass, which does not crystallize, but acts as a solid with relatively mobile atoms until reaction is complete at the sintering temperature. The main problems to date have been the presence of large residual pores and the presence of a small amount of residual glass. Also, the method does not appear to work for any potassium aluminosilicates other than  $\text{KAlSi}_2\text{O}_6$ .

Another solution involves, instead of a reactive sintering route, the use of very fine-grained powders, a method which has been demonstrated in the case of mullite and several oxide ceramics. Initial results showed a pronounced densification when submicron size powders were used (see fig. 6). This effect seemed to be related to a grain-size threshold, and so systematic studies were undertaken to determine if the effect of alumina contamination introduced during milling and the effect of the reduction in size could be separated. This was done by milling for progressive periods of time and weighing milling media so that the degree of contamination was known. Since alumina is stable with potassium aluminosilicates up to temperatures well in excess of the sintering temperatures employed ( $1300^\circ\text{C}$ ), a marked effect of the contamination upon the sintering properties would not be expected. Initial experiments in which commercial fine-grained alumina and alumina from the milling media were sintered, showed that the latter densified less than any of the commercial varieties, and less than the milled aluminosilicates, leading to the conclusion that there is nothing different about the sintering properties of the mill contaminant that would explain the enhanced densification of the milled aluminosilicates. The effort was then made to see if a well-defined particle size effect could be isolated. This was investigated by quantitative particle size analysis of milled powders using an SEM image analysis system. By this method a frequency distribution pattern for the alumina contaminant was obtained which was subtracted from the distribution for the milled powders, thus giving a close approximation to the frequency distribution of the pure milled aluminosilicate patterns. The differences between unmilled, manually ground (nondensifiable), and milled (densifiable) powders are extremely subtle, consisting mainly of the presence of an expanded tail at the coarse end ( $> 1\ \mu\text{m}$ ) of the frequency distribution plot in the case of the unmilled material. While the coarse particles may be volumetrically important if present in more than a few percent, it seems difficult to ascribe the pronounced differences in sintering behavior to differences of this kind. Possibly there are differences at the very fine end of the spectrum not detected with the scanning electron microscope (SEM). Alternatively the densification may be the result of enhanced volume diffusion stemming from defects introduced during milling. There appears to be no x-ray evidence for degradation to the point of structural breakdown however. From a practical standpoint, it is perhaps most significant that potassium aluminosilicate ceramics prepared from finely milled powders, although contaminated with alumina, have strengths nearly three times those prepared by reactive sintering ( $\sim 100\ \text{MPa}$  vs  $40\ \text{MPa}$ ). On another level, if an important role for mechanically introduced defects in these materials can be established, this would have implications for processing of many other materials as well. It is possible that examination of vapor pressures of the milled material would shed some light on the problem.



### Sintering in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> System

In contrast to the potassium aluminosilicates discussed above, crystalline anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) both sinters and densifies readily, regardless of the size of powders employed. This at first seems somewhat puzzling as CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, KAlSi<sub>2</sub>O<sub>6</sub>, and KAlSiO<sub>4</sub> all have similar structures, i.e., all are tectosilicates. Therefore studies were undertaken in an attempt to elucidate further the rather remarkable tendency for "self-densification" exhibited by unmilled stoichiometric anorthite powders.

Pellets of three anorthite powders differing slightly in their preparation (see table 2) were sintered for varying times at 1400 °C. Although differences in average particle sizes were minimal, the effects on sintering kinetics were quite apparent as shown in figure 7. In particular, batch AN-2, with the finest particle size shows the most rapid densification, as might be expected. However, a well defined change in kinetics occurs. A two-stage densification mechanism is proposed for anorthite to explain this break. During Stage 1, grain boundary diffusion is the dominant densification mechanism, aided perhaps by an intergranular phase. Stage 1 continues until all high energy grain boundary orientations have been eliminated, a process aided by the presence of fine particles. Batch AN-1 never reaches this stage of orientational equilibrium, and hence no break in slope occurs. Stage 2 is thought to result from lattice diffusion, perhaps along closely spaced parallel twin planes. Surprisingly, all three end products have similar densities (see table 3, below).

Table 2. Preparation of Anorthite Powders Powder

Powder Batch	Starting Materials	First Homogenization	Calcination	Second Homogenization	Est. Avg. Particle Size
AN-1	Brazilian Quartz + AR Grade CaCO <sub>3</sub> + 0.3 µm Alumina	Ball-Milled 1/2 h	1300 °C 12 h	Ball-Milled 1/2 h	2 µm
AN-2	Brazilian Quartz + AR Grade CaCO <sub>3</sub> + 0.3 µm Alumina	Mechanically Mixed	1300 °C 12 h	Ball-Milled 1 h	1 µm
AN-3	1.5 µm Quartz (0.01 wt. % Fe) + AR Grade CaCO <sub>3</sub> + 0.3 µm Alumina	Mechanically Mixed	1300 °C 12 h	Ball-Milled 1/2 h	3 µm

Table 3. Densities of Sintered Anorthite Powders<sup>a</sup>

Powder	Sintering Conditions	Density, % Theoretical
AN-1	1400 °C, 1000 h	92
AN-2	1400 °C, 1000 h	96
AN-3	1400 °C, 1000 h	94

<sup>a</sup>Measured by adjusting liquid density to the point where the ceramic particle was indefinitely suspended.

The high propensity for pore elimination during sintering shown by anorthite is a desirable, but frequently unattainable, property for ceramic precursor powders. Thus further study of anorthite to elucidate the microscopical reasons for this behavior might prove beneficial in the development of other readily densifiable materials.

#### Ceramic Dielectric Materials

Two of the most potentially economically important problems concerning the electronic ceramics industry are the development of new and/or better compositions for electrolytes for high energy batteries and low dielectric loss/high dielectric constant zero TCK dielectrics for a variety of capacitor applications. These two problems are currently being addressed in this subtask. For ionic conductors current activities are centered around the use of  $\text{Li}^+$  ions in both equilibrium and non-equilibrium oxide phases. The unique qualities provided by the availability of the NBS Reactor dictate that we can make a strong contribution in this area of research as the  $\text{Li}^+$  ions can be located by neutron diffraction but not by x-ray diffraction. Diffraction studies are being conducted in collaboration with Dr. A. Santoro of the NBS Reactor Radiation Division and with an international group of crystallographers (see below). Properties of many of these materials are being evaluated in collaboration with Dr. R. J. Cava. Several different titanate systems are currently being evaluated for their use as zero TCK capacitors. These are either related to  $\text{BaO-TiO}_2$  systems or to  $\text{ZrO}_2\text{-TiO}_2$  systems. Phase equilibria and crystal chemistry of new phases in complex systems containing these titanates are currently being studied. The properties of various ceramics dictated by these studies are being evaluated in collaboration with L. P. Domingues.

A careful study of the data accumulated during the previous year on compositions synthesized in the system  $\text{BaO-Al}_2\text{O}_3\text{-TiO}_2$  indicated that previously published phase equilibria and phase compatibility studies were probably incorrect. An attempt was made to determine the phase equilibria in the nonbinary join  $\text{TiO}_2\text{-BaAl}_2\text{O}_4$ , containing the nonstoichiometric phase  $\text{Ba}_x\text{Al}_{2x}\text{Ti}_{8-2x}\text{O}_{16}$  with the hollandite structure. It was found that at a composition corresponding to an approximate ratio of  $\text{BaO:Al}_2\text{O}_3\text{:TiO}_2 = 2:2:5$  the specimen not only contained no hollandite but also contained no  $\text{BaAl}_2\text{O}_4$ . In fact it contained no phase previously reported to occur in this ternary system. Further experiments proved that two new phases, previously unreported, exist in the system. One of the phases was found



to be C-centered monoclinic with approximate composition 2:3:4,  $2\text{BaO}:3\text{Al}_2\text{O}_3:4\text{TiO}_2$ ,  $\text{Ba}_2\text{Al}_6\text{Ti}_4\text{O}_{19}$ . However, this composition is not known with any great accuracy due to the great difficulty of obtaining single phase specimens which, in turn, is due to the extreme kinetic problems involved in obtaining equilibrium, at temperatures below 1275 °C and the formation of metastable phases. The other compound was also found to be monoclinic C2/m, C2, or Cm with a compositional formula of  $4\text{BaO}:\text{Al}_2\text{O}_3:10\text{TiO}_2$ ,  $\text{Ba}_2\text{Al}_2\text{Ti}_{10}\text{O}_{27}$ . A specimen of this composition was prepared and found to be single phase. In view of the occurrence of the two previously unrecognized phases the phase equilibrium diagram of this system has been reevaluated and the revised version is shown in figure 8.

A new program to investigate the physical and dielectric properties of  $\text{ZrTiO}_4$  and  $\text{ZrTiO}_4$ -based solid solutions has been initiated. The research is stimulated by current technological interest in  $\text{ZrTiO}_4$ -based ceramics as dielectric resonator materials in microwave devices. The practical application of these materials is presently hindered by incomplete information on the chemistry and structure of  $\text{ZrTiO}_4$  and of  $\text{ZrTiO}_4$ -based solid solutions.

A study to determine the temperature of the high-low transition in  $\text{ZrTiO}_4$  has been completed, together with a preliminary study on the effect of substitutional tin on the phase transition behavior. Zirconium titanate has been shown to have a unique and previously unreported phase transition most clearly shown in the dependence of the c-axis length of the orthorhombic (Pcnb) unit cell on temperature as seen in figure 9. The unit cell volume decreases linearly with decreasing temperature between ~ 1480 and the "true" phase transition at  $1125 \pm 20$  °C, apparently continuing to decrease at lower temperature. The maximum unit cell dimensions are  $a = 4.806$ ,  $b = 5.035$ , and  $c = 5.498\text{\AA}$  and are found only at  $T > 1480$  °C. The minimum unit cell dimensions, achieved only by very slow cooling and equilibration at ~ 750 °C were found to be  $a = 4.828$ ,  $b = 5.035$ , and  $c = 5.348\text{\AA}$ .

The unit cell dimensions observed for  $\text{ZrTiO}_4:\text{SnO}_2$  solid solutions did not exhibit strong temperature dependence,  $\text{SnO}_2$  in solid solution apparently being effective in stabilizing the random nature of the high temperature  $\text{ZrTiO}_4$  structure type.

Flux grown single crystals of  $\text{ZrTiO}_4$  have been prepared at temperatures both above and below the phase transition. The structure of these crystals is presently under investigation. Initial studies indicate the presence of a-axis superstructure in the low temperature phase which is not present in crystals quenched from above the phase transition temperature. The relationship of this observed superstructure to extra lines observed in x-ray powder patterns of low temperature  $\text{ZrTiO}_4$  is not clear. Neutron diffraction studies both high and low temperature forms of  $\text{ZrTiO}_4$  have been initiated with the cooperation of Dr. A. Santoro of the NBS Reactor Radiation Division which are expected to yield better information on the details of anion packing in the structure as relating to the observed "extra" spots and lines seen in x-ray diffraction patterns.

This work has indicated a need for characterization of the dielectric properties of the "true" high and low temperature phases of  $\text{ZrTiO}_4$ .



Studies are proceeding on methods for the low temperature synthesis of high quality ceramic powders suitable for sintering at temperatures to produce either high or low temperature structure type. The cooperation of L. P. Domingues has been obtained for the dielectric characterization of these specimens as they are prepared. Similarly prepared  $\text{ZrTiO}_4$ -based solid solutions will be systematically examined to determine the effects of substitutional cations on the physical and dielectric properties of technological importance for application in dielectric resonator devices.

Interest in  $\text{Li}_2\text{O}$  containing phases has been greatly stimulated by the possibilities of  $\text{Li}^+$  ion conduction in such phases for use as a solid electrolyte in lightweight, high energy battery systems. The phase equilibria and crystal chemistry of systems combining  $\text{Li}_2\text{O}$  and tetravalent and/or pentavalent metal oxides is largely unknown. Studies on the crystallographic properties of  $\text{Li}_2\text{SnO}_3$  and  $\text{Li}_2\text{ZrO}_3$  have been completed during FY82. In addition, our study of the high temperature form of  $\text{LiTa}_3\text{O}_8$  has been completed. Single crystals of  $\text{LiTa}_3\text{O}_8$  prepared by W. S. Brower (deceased) were examined in Grenoble to determine the true unit cell dimensions and symmetry. A Weissenburg film camera was used on the Grenoble neutron diffraction equipment to give a picture that revealed extra rows of diffraction spots indicating a superstructure with a doubled 'b' axis ( $3.8\text{\AA} \times 2$ ). This superstructure is not visible at all by x-ray diffraction even with very long exposure time although there is some indication of the doubled cell in electron diffraction patterns. A structure refinement of the single crystal neutron diffraction data has revealed that the  $\text{Li}^+$  ions are ordered in two different sets of coordination polyhedra in each of the units of the doubled cell. Rietveld refinement of the powder data does not clearly lead to unambiguous ordering parameters. In this case single crystal neutron diffraction is the only technique which has unambiguously led to the correct determination of the position of the  $\text{Li}^+$  ions in an oxide structure. Data should be collected and refined from single crystal neutron diffraction equipment operating at high temperatures to determine the exact mechanisms. These experiments are under consideration at the present time at both NBS and at Grenoble.

Further studies have continued on the synthesis, conductivity, and structure refinement of various  $\text{Li}^+$ -intercalated (or  $\text{Li}^+$ -inserted) transition metal oxide phases in collaboration with Dr. R. J. Cava. Considerable progress has been made in the characterization of  $\text{Li}^+$ -insertion phases related to the Wadsley-Roth block structures originally reported in  $\text{Nb-O}$ ,  $\text{Nb-Ti-O}$ ,  $\text{Nb-W-O}$ , and  $\text{W-V-O}$  systems.

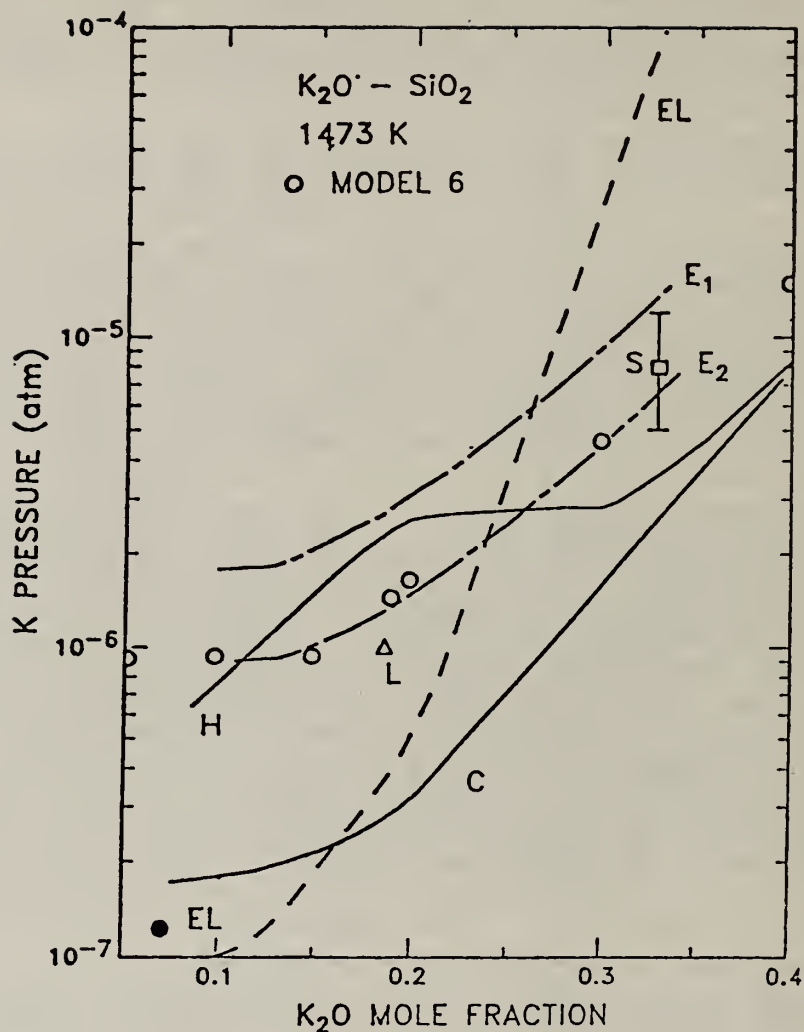


Figure 1 Potassium pressure dependence on total  $K_2O$  mole fraction for the binary  $K_2O-SiO_2$  system. Curve  $E_1$  is the experimental curve of Plante (1979) and curve  $E_2$  is the corresponding lower limit based on temperature, pressure, and composition uncertainties. Curve C is that of Charles (1967) based on a combination of Preston and Turner's (1933) transpiration data and phase diagram analysis. The curve labeled EL and the closed circle are based on experimental and estimated data of Eliezer et al. (1978) and the Redlich-Kister equation. The open square point S is calculated from the Spencer et al. (1975)  $\Delta G_f$   $K_2Si_2O_5(l)$  data and Charles'  $SiO_2$  activity with the error bar reflecting the  $\Delta G_f$  uncertainty only. The triangular point was calculated by Spacil and Luthra (1980) from the phase diagram.

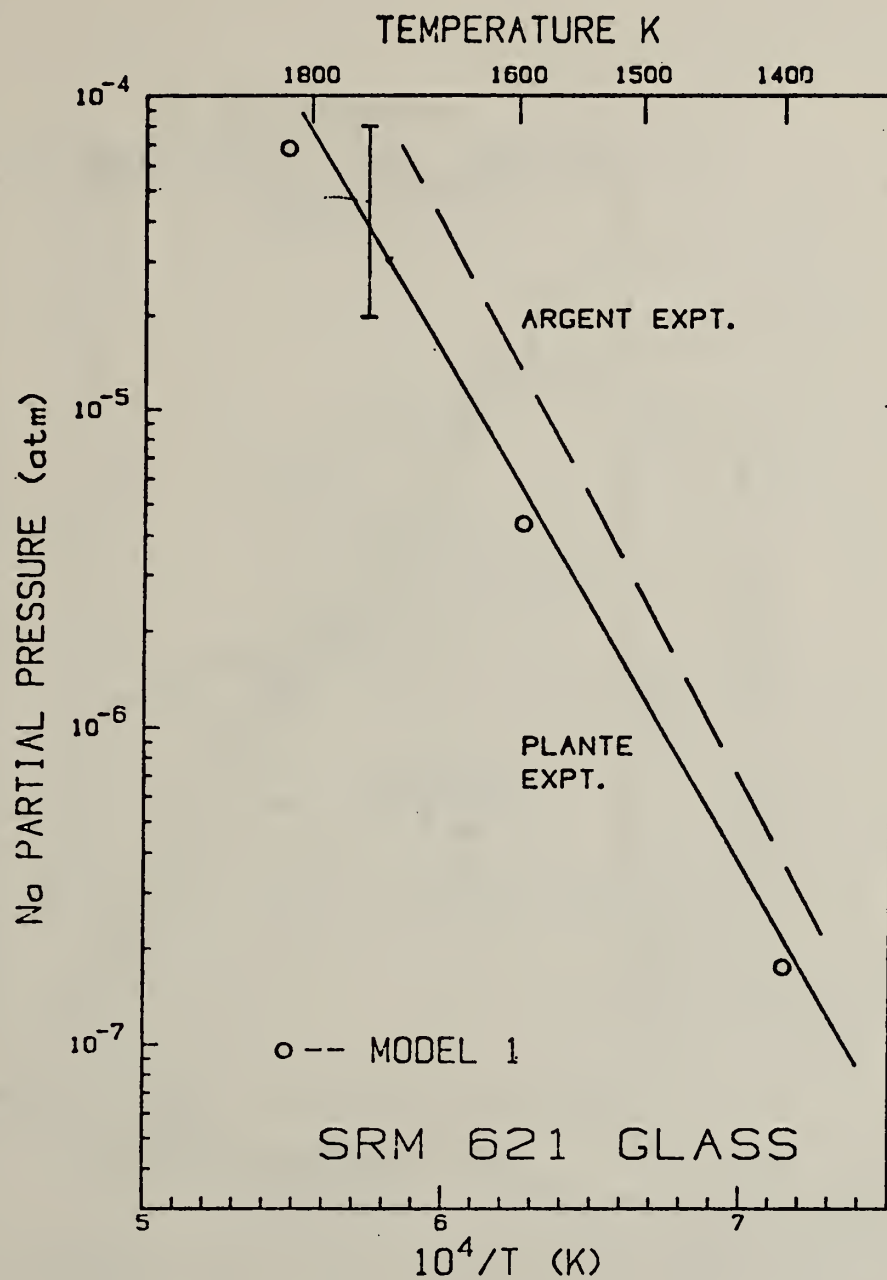


Figure 2 Comparison of model (open circles) and experimental Na-partial pressures over SRM-621 glass (see table 1).



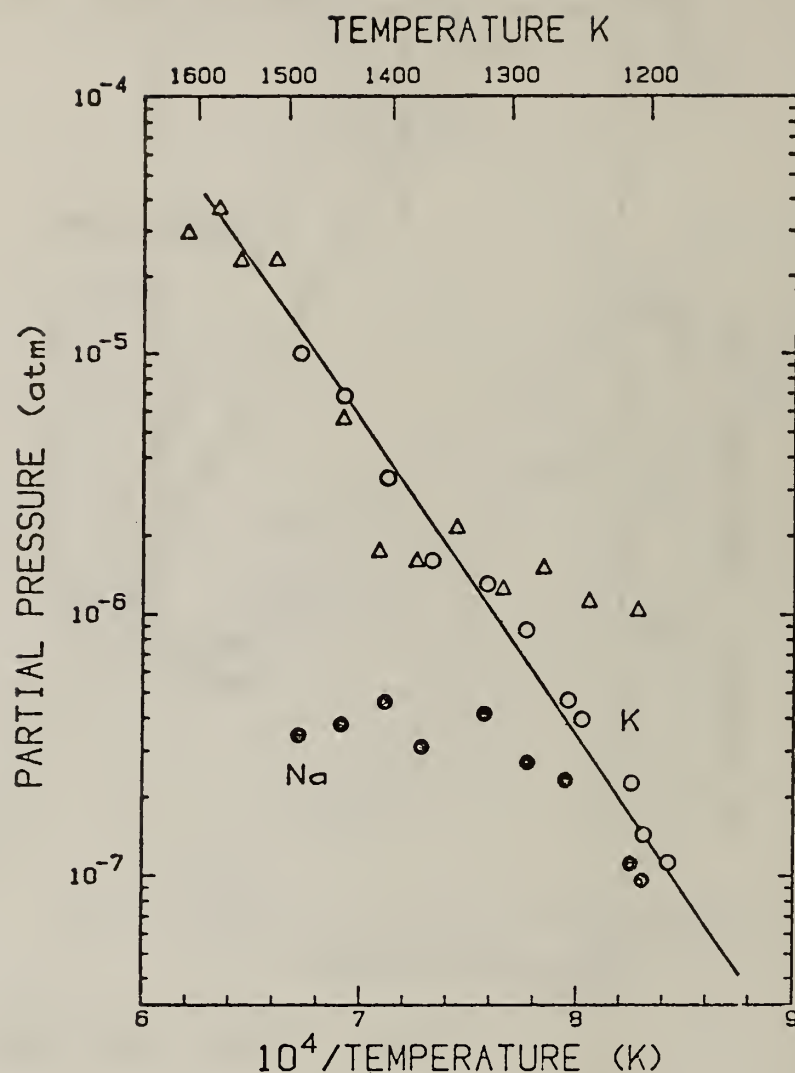


Figure 3 Partial pressures of K and Na as a function of reciprocal temperature for dolomitic limestone with wt. % composition: CaO (30.1), MgO (21.3), SiO<sub>2</sub> (1.2), Al<sub>2</sub>O<sub>3</sub> (0.19), Fe<sub>2</sub>O<sub>3</sub> (0.28), Co<sub>2</sub> (46.6), K<sub>2</sub>O (0.12), Na<sub>2</sub>O (0.01), SrO (0.01), MnO (0.03), and TiO<sub>2</sub> (0.02). The solid curve represents the best fit to the Knudsen K pressure data (open circles); triangles represent TMS K-pressure; and closed circles represent KMS Na-pressure.

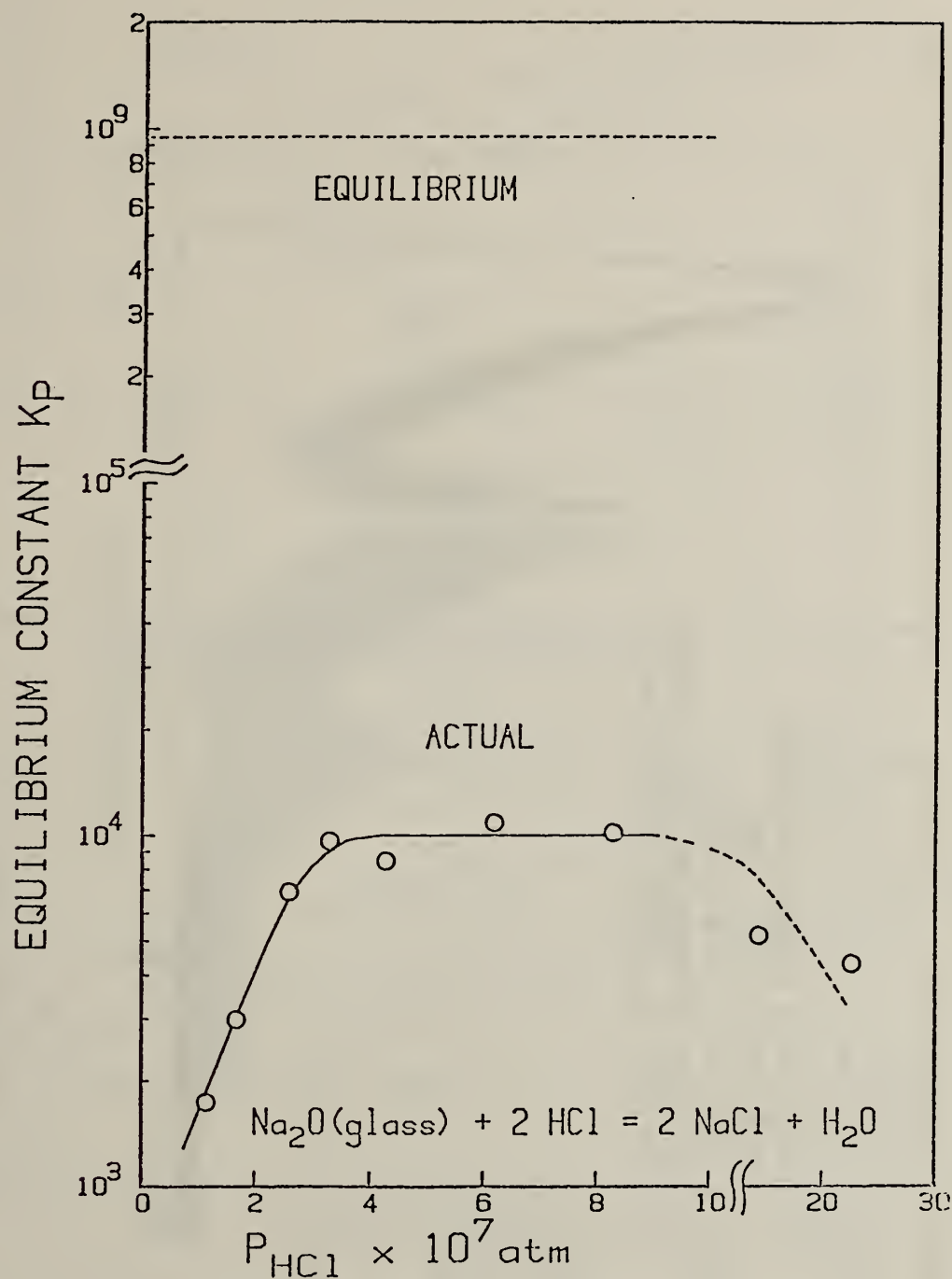
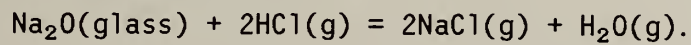


Figure 4 KMS data for the apparent equilibrium constant as a function of HCl pressure for the system,



# TEMPERATURE DEPENDENCE OF NITROGEN RAMAN SPECTRA

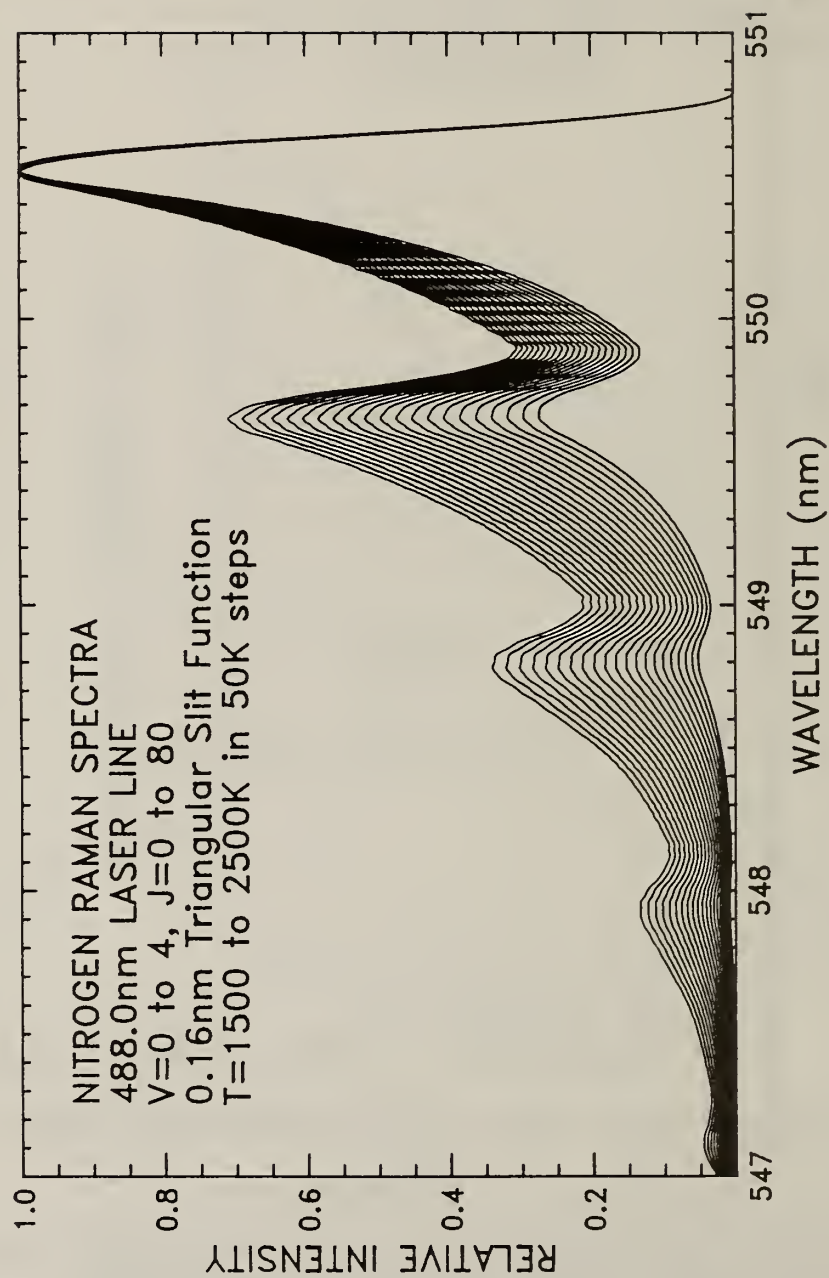


Figure 5 Calculated Raman spectra for  $\text{N}_2$  as a function of temperature.



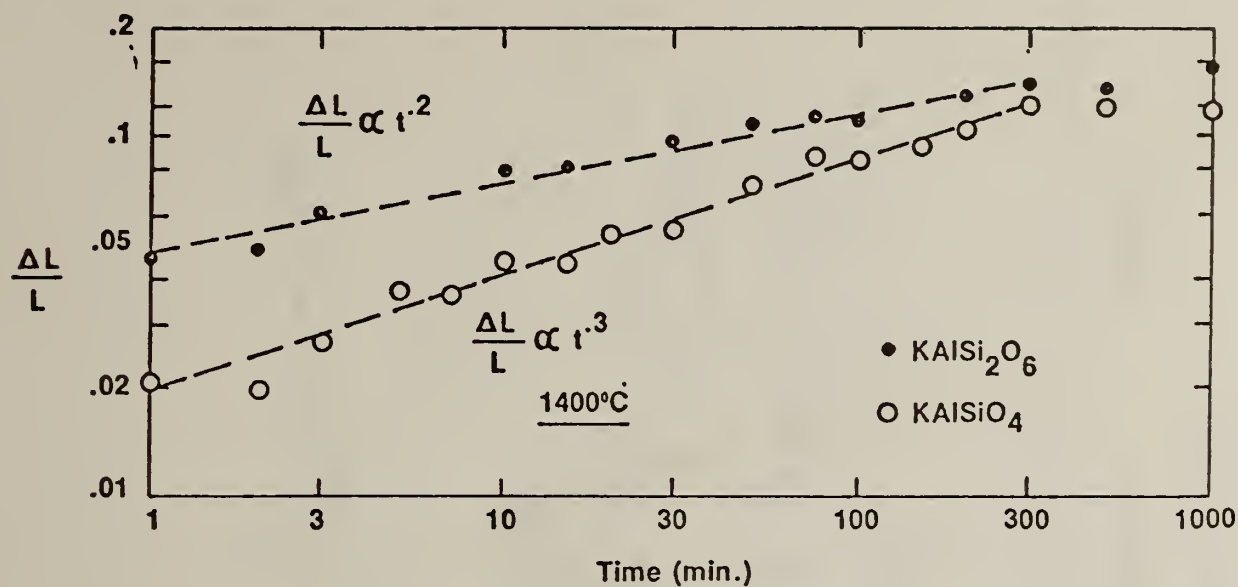


Figure 6 Shrinkage ( $\Delta L/L$ ) vs time (log/log) plot for  $0.5 \mu\text{m}$  powders produced by extended ball-milling.

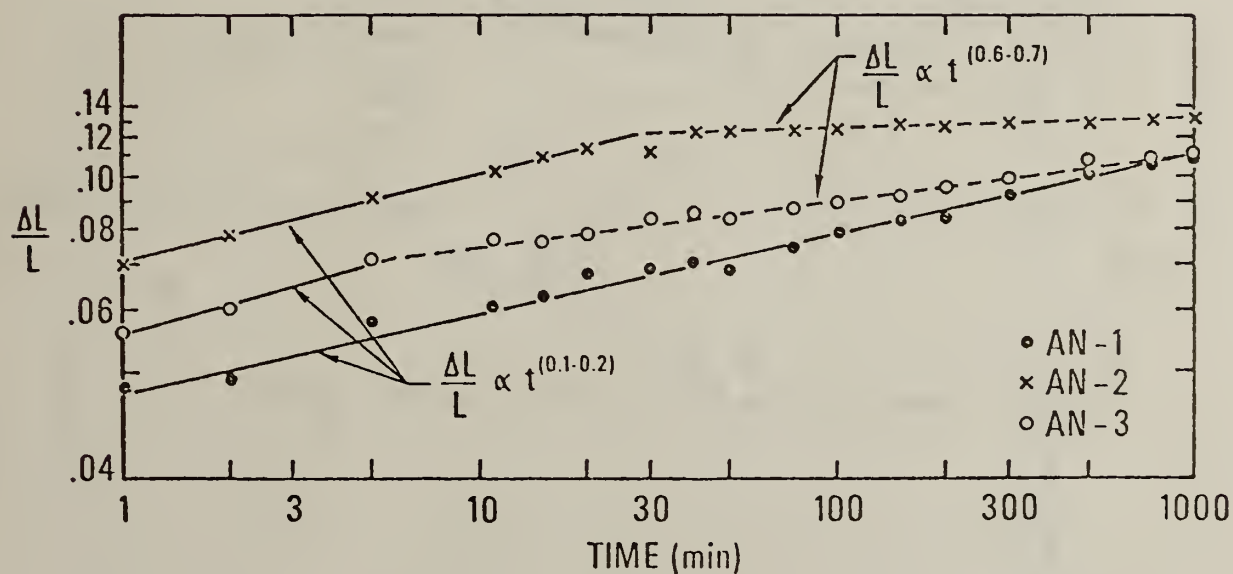


Figure 7 Shrinkage vs sintering time at  $1400^\circ\text{C}$  for three anorthite powders (log/log plot).

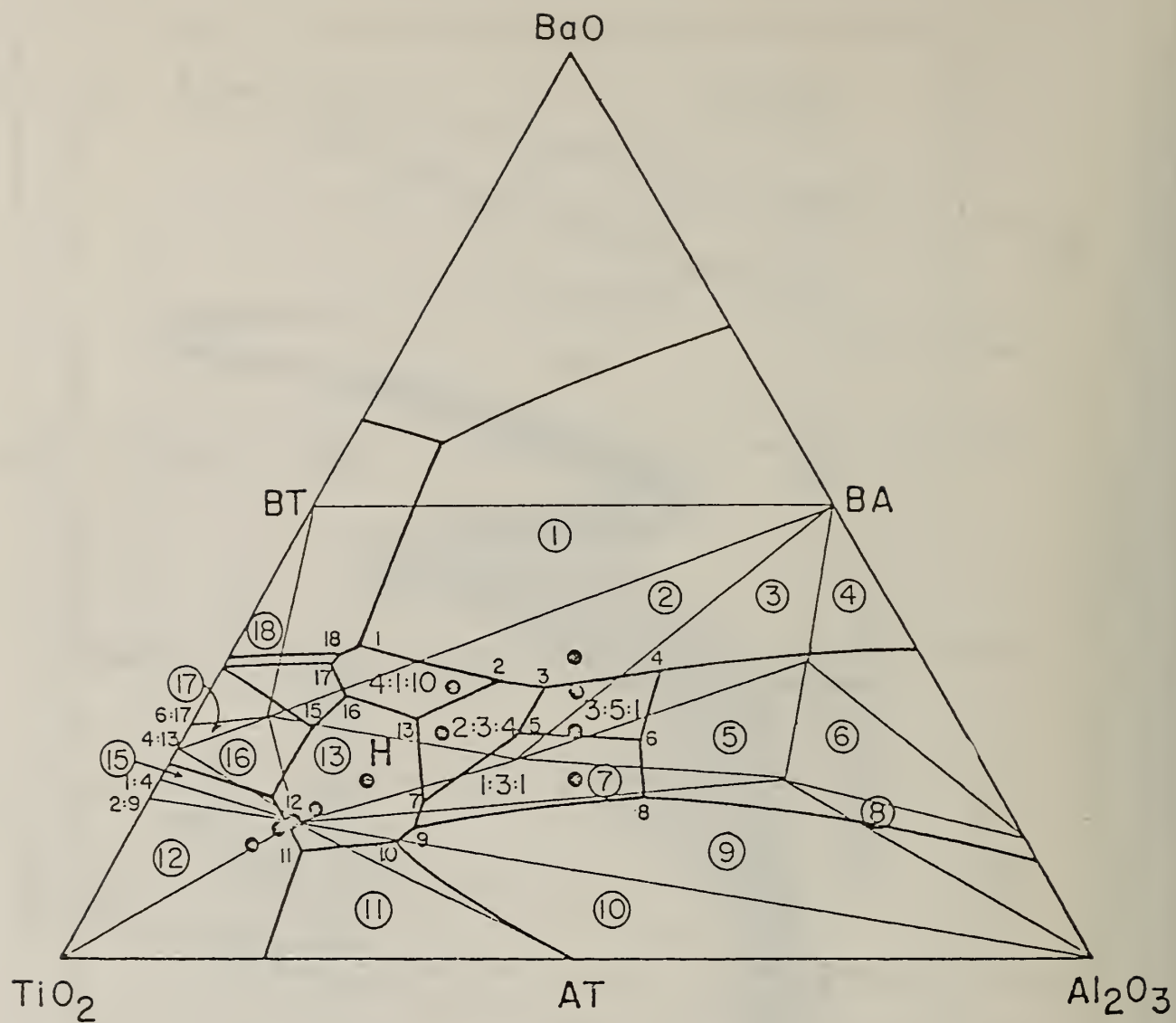


Figure 8 Phase diagram for the BaO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system.

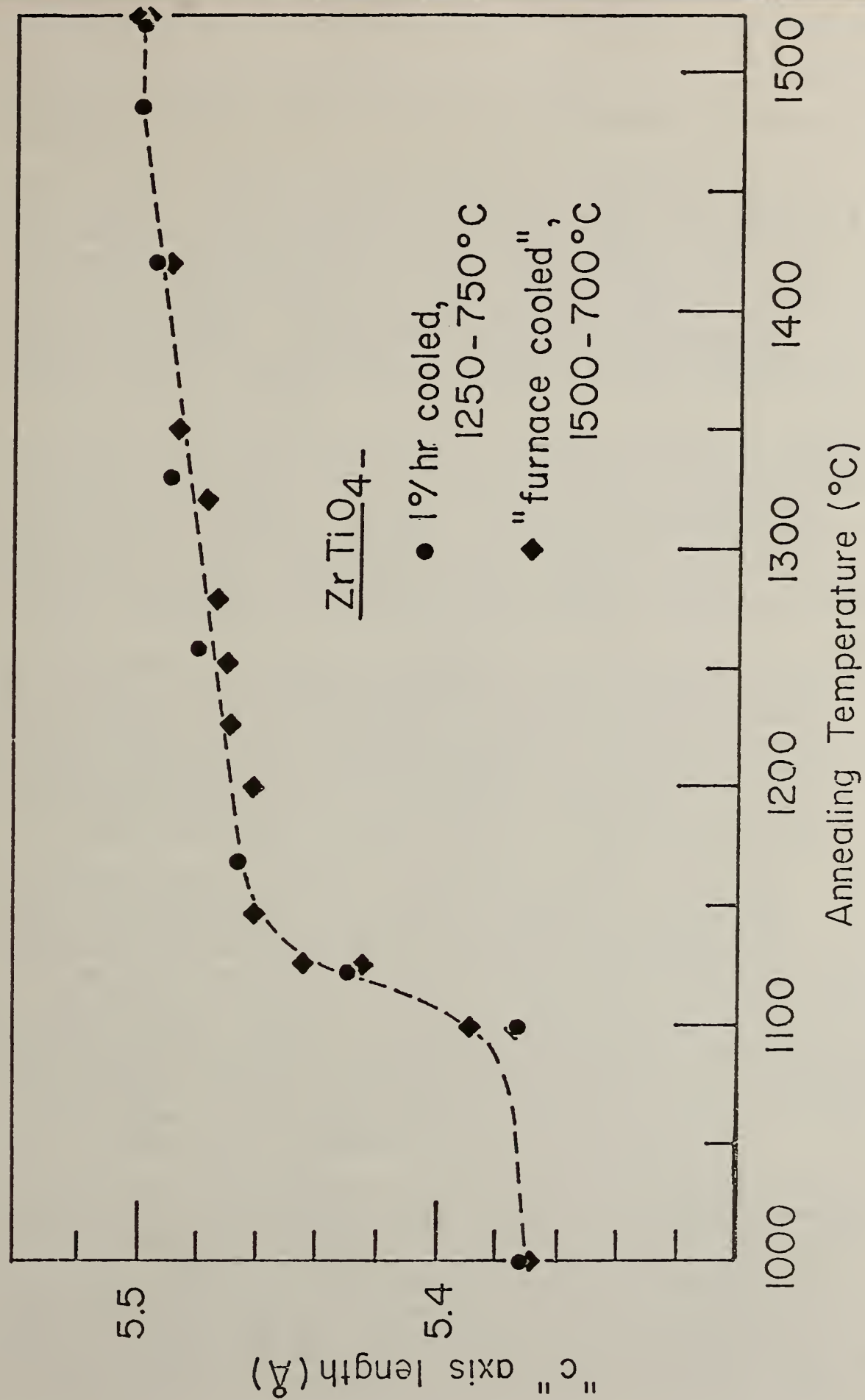


Figure 9 Phase transition for  $\text{ZrTiO}_4$ .





## PROPERTIES, STRUCTURE, AND STANDARDS FOR GLASS AND OPTICAL MATERIALS

### Task 12154

Glass is a solid material, characterized by an unique combination of properties and a distinct production technology. It is the product of a large, well-focused world-wide industry. With respect to production technology, thermo-plasticity is the most unique physical property of glass. It allows the production of glass objects by such high-speed processes as casting, blowing, pressing, centrifugal casting, spinning, drawing, and slumping. Although made from relatively abundant and inexpensive materials, manufacture of glass requires high temperature processing with its inherently costly problems of furnace corrosion, air pollution, and fuel economy.

Unique user-related properties of glass are optical transparency, chemical durability and low thermal and electrical conductivity. These properties are the basis of the major bulk uses of glass which are architectural glazing, optical components, containers, enamels, building insulation, and electronic components. More novel applications of glass are solar energy devices, lasers, fiber-optic devices, hosts for nuclear waste, electronic substrates and insulation layers, computer displays, pH-sensors, and several more defense and national security related applications.

The Glass Group is involved in the generation of basic scientific data which relate to such fundamental processes as glass formation, glass crystallization and phase separation. Such data are used by industry and researchers throughout the world as guidelines for the development of glasses located within glassforming boundaries, while having combinations of useful properties. This research, accomplished in part in collaboration with guest workers and outside laboratories, is described in more detail below under Subtask 1 (Physics and Chemistry of Glass).

In other activities of Subtask 1, the Group is further involved in studying fundamental properties such as propagation of light under conditions of pressure or in the multiple internal reflection mode encountered in planar wave guides. The wave-guide mode was used to measure thickness and refractive indices of glassy thin films synthesized by co-deposition from molecular beams, confirming the applicability of principles of glass formation. This study, aside from contributing to the basic understanding of glass formation, promises also to yield novel films without the deleterious effects of grain boundaries (light scattering, chemical attack). The thin film synthesis and analysis facility designed for this purpose has since found other uses which are described in Subtask 5 (Preparation and Characterization of Thin Films).

The Glass Group of the NBS has a long tradition of close relation with the U.S. glass industry through personal contacts and through the American Society for Testing and Materials (ASTM) Committees on which representatives of the industry and members of the Glass Group are seated. Much of the work of the Group reflects therefore directly the needs of the glass-producing and glass-using industries. Activities in Subtask 2 (SRMs for the glass industry) relate directly to glass properties of interest to glass production (e.g., viscosity, high temperature resistivity) or to glass usage (e.g., dielectric constant, thermal expansion). This

year, certification activities for a dielectric constant glass standard were completed. This standard will aid the glass as well as the electronic industry, which uses glass for a great variety of transparent and/or insulating components.

An activity which arises both from the NBS's major mission in standards and the Group's ability to synthesize glasses of unusual compositions is the development of glass-based standards which benefit industries other than glass producers or glass users. Glass, as a solidified liquid, permits production of large pieces of solids, having an inspectable homogeneity not available from other materials. Its unique structure permits compositions spanning a wide range of stoichiometries. Furthermore, such homogeneous glasses can be easily formed into many shapes, ranging from bulk pieces, fibers and microspheres to films, disks, and cubes. Such SRMs, made by the Glass Group, generally serve analytical-chemical purposes, but are also calibrated for such properties as optical fluorescence. Activities of this kind are described in Subtask 3 (Glass Standard Reference Materials for Other Industries). A recent addition to glass-based analytical standard materials are glasses for calibration of biological tissue analyzers where certain normal and abnormal tissue-elements are incorporated into a low Z-glass matrix.

The NBS Glass Group is well known for its ability to solve glass synthesis problems, particularly if they relate to developing glasses with properties which are difficult to achieve, and/or to measure. Such activities, listed under Subtask 4 (Special Glass Developments), are usually carried out in response to requests from other government agencies. In some cases these agencies not only seek special expertise, but also wish to retain NBS scientists as neutral experts where large expenditures or critical decisions are involved. A noteworthy development for this year are novel glasses having unusual combinations of high modulus of elasticity and low thermal expansions. These glasses promise to be good candidates for forming the outer layer of composite glass fiber sensor leads, protecting the signals in the fiber from spurious modulating due to external pressure changes. Such fibers are desired for deep-sea applications such as hydrophones and data links.

The Glass Group continues to respond to a large number of glass-related inquiries from the glass-using, glass-producing industry, the general public, government agencies, universities, and research laboratories which look upon NBS as a national focus in glass technology. The inquiries reflect to a certain extent national trends. Inquiries during the last year covered such subjects as automotive safety devices, glass for electronic microchips, solar energy devices, glass fibers for building insulation, accidents involving glassware, and military infrared detectors and accessories. Members of the Glass Group were also requested to review export licenses for glass-related products and/or for technical know-how of potentially strategic importance. A study of failures of architectural glass components and their safety was undertaken for the Architect of the Capitol.

Technical activities for each Subtask are described below.



Physics and Chemistry of Glass  
Subtask 1 of Task 12154

D. H. Blackburn, D. J. Cronin, A. Feldman, L. H. Grabner, W. K. Haller, D. A. Kauffman, D. M. Sanders, R. M. Waxler, and C. M. Scarfe<sup>1</sup>

<sup>1</sup>Guest Worker from the University of Alberta

Nucleation Kinetics in  $\text{Li}_2\text{O}-2\text{SiO}_2$  Glass

The nucleation and crystallization of melts is a topic of continuing interest in glass technology since it controls glass formation and can also be used to produce dense fine-grained ceramics of commercial importance. A study of heterogeneous nucleation behavior in  $\text{Li}_2\text{O}-2\text{SiO}_2$  glass was undertaken in an effort to obtain a better understanding of the nucleation process.  $\text{Li}_2\text{O}-2\text{SiO}_2$  was chosen for several reasons. It is a simple glass yet forms the basis for commercially important glass ceramic materials. This particular composition has frequently been used in nucleation studies and has been well characterized with respect to homogeneous nucleation. These results have shown that over the entire nucleation range classical nucleation theory does not adequately describe the nucleation behavior. This is in contrast to other simple silicates which behave according to classical nucleation theory.

Experimental results reported in the literature on  $\text{Li}_2\text{O}-4\text{SiO}_2$  using platinum as a nucleation catalyst show a maximum in a plot of volume percent crystal versus platinum content. Preliminary measurements at NBS showed similar behavior for  $\text{Li}_2\text{O}-2\text{SiO}_2$  glass. No adequate explanation for this effect has been given. Therefore, to clarify this point and provide accurate heterogeneous nucleation data for  $\text{Li}_2\text{O}-2\text{SiO}_2$  as a test of classical nucleation theory and as a comparison with homogeneous nucleation data a detailed study of nucleation in the  $\text{Li}_2\text{O}-2\text{SiO}_2$  glass was carried out.

Due to the catalytic activity of the platinum particles in bringing about crystallization, a new technique had to be developed to determine the number of crystals formed in a given time period. Normally this is done by nucleating at a given temperature after which the sample is taken to a higher temperature to grow the nuclei to an easily observable size. This requires that the nucleation rate vs temperature, and crystal growth rate vs temperature curves being separated so that there is no nucleation at the growth temperature.

The effectiveness of platinum particles in nucleating crystals in  $\text{Li}_2\text{O}-2\text{SiO}_2$  glass causes a shift of the nucleation rate curve to higher temperature, making the usual technique of obtaining nucleation data unusable.

The technique developed requires measuring the size distribution of crystals in the glass and the crystal growth rate at the temperature used. The number of crystals formed at any time can then be determined. The various nucleation parameters can be evaluated by fitting the data to the appropriate equations for nucleation.

It is also of interest to compare the number of crystals formed with the number of available heterogeneous sites to determine if indeed all sites produce crystals. A method was developed where the platinum particles can be separated from the glass and the total number of particles/unit volume of glass can be determined. The results show that there is good agreement between the number of crystals found and the number of platinum particles available, indicating that all particles are actual nucleation sites.

Scanning electron microscopy examination of the early stages of crystallization showed that after etching with a weak hydrofluoric acid (HF) solution a thin layer of material at the platinum interface has been removed. One possible explanation is the presence of lithium metasilicate as the initial phase formed. Such a reaction has been suggested in the literature on the basis of indirect evidence. Other investigations report no sign of  $\text{Li}_2\text{O} \cdot \text{SiO}_2$  during the crystallization of  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ .

High precision x-ray diffraction analysis, carried out at Alfred University, has shown the presence of small amounts of  $\text{Li}_2\text{O} \cdot \text{SiO}_2$  phase during the early stages of crystallization. This is the first direct evidence for this effect. This requires a re-evaluation of the analysis of nucleation data to include this reaction.

#### Viscosity of Melts in the $\text{CaO-MgO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ System

This work is being carried out in collaboration with Dr. C. M. Scarfe of the University of Alberta, Canada.

Melt-viscosity is an important property of glasses, both from the scientific and the technological standpoint. The viscosity is an expression of the melt structure and in particular of associated or polymeric states which appear to be a prerequisite for easy glass formation. The current work involving viscosity measurement along the diopside ( $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ )-albite ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ) join is an extension of earlier work on the diopside-anorthite ( $\text{CaO-Al}_2\text{O}_3\text{-}2\text{SiO}_2$ ) binary. These systems are of interest to glass technologists and geologists for data obtained on specific compositions but also for the knowledge that can be gained on the general behavior and structure of silicate melts.

The work on the diopside-anorthite system has been described in a paper which has been submitted for publication in American Mineralogist.

The results on the diopside albite system show an increase in viscosity at constant temperature as albite is substituted for diopside. This involves an increase in  $\text{SiO}_2$  in the melt as well as  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  replacing  $\text{CaO}$  and  $\text{MgO}$ . In terms of structure this is viewed as moving from a depolymerized structure to a three dimensional network type structure. The rate of change of viscosity increases going from diopside to albite. Further interpretation of the viscosity data and correlation with structural information gained from vibrational spectroscopy will be carried out in the near future.

The high temperature viscosity data obtained for the melt of albite agree well with values in the literature. Literature values for the low



temperature, 800 to 1000 °C, viscosity data, however, show considerable disagreement. The viscosity of albite will be measured in this temperature range in an attempt to clarify the situation.

#### Vapor Co-deposition Pathways to Dense Glass-like Solids

The traditional way of forming glasses by undercooling of melts is not the only way to produce dense amorphous solids. We are exploring the production of glass-like structures by co-deposition from the vapor phase. This study has general interest for the process of glass formation. In addition, it has some important practical implications. Currently the weakest parts of high-energy laser systems for military and energy applications are the reflection and antireflection coatings which fail when subjected to high energy pulses. The magnitude of such pulses is significantly lower than can be transmitted through the bulk glass elements. The exact mechanism for the failure is still poorly understood, but there is growing evidence that the presence of grain boundaries is at least partly responsible. Films produced in our study are free of grain boundaries and it is hoped that such films may have improved hardness to high energy laser damage.

In earlier work by our Group, adding 19 mol %  $\text{SiO}_2$  to a  $\text{ZrO}_2$  matrix produced a film which was amorphous as determined by x-ray diffraction and scanning electron microscopy. Silica was chosen because it is a well-known glass-former in bulk glass formulations. The requirement of using a traditional glass-former, however, restricts the possible values of index of refraction for resulting mixed films. This restriction is particularly severe for applications requiring high index of refraction. For this reason, the effects of adding a non-glass forming component ( $\text{MgO}$ ) to a  $\text{ZrO}_2$  matrix was studied. Based upon examination by x-ray diffraction it appears possible to produce glassy films using a mixture of non-glass-formers. However, the concentrations of required additions are higher (50 mol %) and the probable mechanism for glass formation is different. These results are discussed in more detail in a SPIE Proceedings article based on a talk given in Arlington, VA, in May 1982. In addition to exploring the influence of crystallinity on laser damage resistance, we have a longer-term goal of producing gradient index antireflection coatings by coevaporation. As discussed in the section "Preparation and Characterization of Thin Films" below, the capability of producing gradient refractive index coatings by computer-controlled coevaporation is under development. Since such coatings can, in theory, eliminate the abrupt breaks in the refractive index found in currently employed antireflection layered structures, they may have increased resistance to high-energy laser damage.

Finally, we are currently calibrating the electron spectroscopy for chemical analysis (ESCA) facility to permit an accurate quantitative analysis of mixed oxide films. This will allow rapid comparison of the mixed vapor concentration with the concentration of the resulting thin films. Such a comparison should prove useful in determining if preferential bonding occurs in the film. Clustering has been observed by other workers using field ion microscopy and is highly significant in explaining breaks in property curves in bulk glass-forming systems.



## Dynamic Synchrotron SAXS Investigation of Subliquidus L/L Phase Separation in Glasses

This is a collaborative project between the Stanford Synchrotron Radiation Laboratory (SSRL) and the NBS.

Phase separation is an important phenomenon in glass formation and the precise kinetics and mechanisms are still not fully understood. Most understanding so far has come from studies on phase separated melts which were chilled to freeze the structures and to make them observable with such techniques as electron microscopy. The high x-ray intensities available from synchrotron sources opened the possibility for in situ studies of the early stages of phase separation.

Time-resolved small angle x-ray scattering (SAXS) studies were first performed on  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  glasses. These glasses scattered relatively weakly but demonstrated the ability of the SAXS system for investigating the phase separation. The change in the SAXS pattern recorded every few seconds could be readily monitored as the sample temperature was manipulated and the composition inhomogeneities grew or dissolved. It was found, however, that the scattering from the borosilicate samples was not reproducible as they were repeatedly cycled above and below the miscibility temperature. This was attributed to composition drift due to preferential evaporation.

To improve on the contrast in the glass, it was decided to develop phase separating compositions containing heavy elements such as BaO. Promising compositions in the  $\text{BaO}-\text{K}_2\text{O}-\text{SiO}_2$  (BKS) system were located. Although it was difficult to produce homogeneous samples of glasses with compositions close to the line of critical points of the metastable immiscibility dome (due to high viscosities at achievable temperatures), homogeneous samples were made of compositions with slightly less silica. Several major improvements were made to the SAXS detector system. To provide compatibility with existing facilities at SSRL, the hardware and software were modified for use with a PDP11 computer. An unscreened 1024-pixel Reticon photodiode array, which absorbs x-radiation directly in the photodiodes, was installed as the sensing element in place of the phosphor/fiber-optics-covered array used previously. This resulted in an order of magnitude improvement in sensitivity, giving an instrumental noise equivalent to less than 3 (9 keV) photons/pixel/readout and saturation at around 5000 photons/pixel/readout. The extra sensitivity improved the quality of the data obtainable during the earliest stages of phase separation when scattering was very weak.

Experimental runs with a  $\text{BaO}-\text{K}_2\text{O}-\text{SiO}_2$  glass showed that the scattering during early-stage phase separation was intense enough to characterize the process and was reproducible. A redesigned sample furnace was installed to minimize temperature gradients in the sample. Data were obtained for two compositions ( $\text{BaO}:0.05, \text{K}_2\text{O}:0.05, \text{SiO}_2:0.90$  and  $\text{BaO}:0.06, \text{K}_2\text{O}:0.06, \text{SiO}_2:0.88$  mole fractions) at several holding temperatures. The absolute efficiencies of the array and incident intensity monitors were measured so that the data may be expressed in units of differential cross-section per unit sample volume for comparison with theory. Analysis of the data and system documentation are presently underway.

## Piezo-optics

Relatively few piezo-optic measurements have been made at wavelengths above 2.5  $\mu\text{m}$  and most of these data are at discrete laser wavelengths. With so few data it becomes difficult to test any of the theories that have been developed for predicting photoelastic dispersion due to the effect of strain on the infrared-active transverse-optic (IRTO) phonon. This is in contrast to the relative success of fitting piezo-optic data to strain-induced electronic effects such as the effect of strain on the energy bands and free carriers of semiconductors. Only recently have piezo-optic measurements been made at a significant number of wavelengths and most of these measurements have been made at this laboratory. This year we have performed piezo-optic measurements on  $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{SrF}_2$ , GaAs, and  $\text{CdF}_2$ . Almost all of these materials are technologically important as infrared transmitting materials.

In our earliest work we had reported on room temperature measurements of all the piezo-optic constants  $q_{11}$ ,  $q_{12}$ , and  $q_{14}$  of  $\text{CaF}_2$  and  $\text{SrF}_2$  at the discrete laser wavelengths 0.6328  $\mu\text{m}$  and 3.39  $\mu\text{m}$ . In later work we had extended the piezo-birefringence measurements further into the infrared where we observed a large dispersion due to the proximity of the IRTO phonons. The data had been fitted to a three parameter oscillator model based on the strain dependence of the IRTO phonon frequency and oscillator strength.

Most recently, a sensitive detector became available to us so that improved measurements could be made in the wavelength range 5.5 to 11.0  $\mu\text{m}$ . We therefore repeated the piezo-birefringence measurements at more wavelengths in this range. The results were generally in good agreement with our earlier measurements. All the data have been fitted to an improved model of piezo-birefringence originally presented by Humphreys and Maradudin and subsequently by Bendow, Gianino, Tray, and Mitra. We find that the principal contribution to the dispersion comes from the strain-induced splitting of the IRTO mode. Estimates have been made of the strain-induced relative anisotropy of the transverse effective charge. Although the data can be fit to the basic phenomenological model of HM, no microscopic theoretical calculations are available to compare with the computed parameters. Such calculations have been made for GaAs and, hence, similar measurements have been conducted on GaAs; the measurements and these analyses were discussed in the previous annual report.

Because of the similarity of the infrared absorption spectrum of  $\text{CdF}_2$  with that of  $\text{CaF}_2$ , we decided to measure the infrared piezo-birefringence of  $\text{CdF}_2$ . Crystals of  $\text{CdF}_2$  were purchased from a commercial supplier. Two specimens were prepared from these crystals, one oriented for stress along the [001] crystal axis, the other for stress along the [111] crystal axis. The [001] specimen was a rectangular prism approximately 6 x 7 x 17 mm; the [111] specimen was a rectangular prism approximately 8 x 8 x 22 mm.

The refractive index of  $\text{CdF}_2$  was measured at nine wavelengths in the visible and at 1.15  $\mu\text{m}$  by means of a V-block refractometer. The data



were fitted to a power law expression of the form  $n^2 = A\lambda^2 + B + C\lambda^{-2} + D\lambda^{-4} + E\lambda^{-6} + F\lambda^{-8}$  with a standard deviation of  $1.4 \times 10^{-4}$ . A fit to the above equation was also obtained by eliminating the point at  $1.15 \mu\text{m}$ ; the coefficients changed in value and the resultant standard deviation was  $7 \times 10^{-6}$ . The measured values differed by 0.005 from values reported in the literature; this difference is attributed to differences in crystal purity.

The piezo-optic constants  $q_{11}$ ,  $q_{12}$ , and  $q_{14}$  have been measured in the visible at  $0.6328 \mu\text{m}$ . The coefficients show a considerable dispersion in the infrared which follows closely the dispersion of the corresponding coefficients of  $\text{CaF}_2$ .

#### Propagation, Attenuation, and Thickness Measurements in Thin Films

The refractive index and thickness of a film prepared by coevaporation (79%  $\text{MgO}$ , 21%  $\text{SiO}_2$  by volume) was measured by the prism coupler method. Measurements of the transverse electric (TE) and transverse magnetic (TM) mode coupling angles were made at three wavelengths of the argon-ion laser. Computer programs were developed for fitting the prism coupler data to the thin film mode propagation equations in order to calculate the refractive index and thickness of the film. The prism coupler method is a very precise means for obtaining the refractive index of thin films. Thus we were able to measure dispersion in the refractive index; furthermore, the accuracy was sufficient to measure a birefringence on the film which we attributed to internal stresses. A signature for the birefringence was observed in the m-line spectrum of the film, in which the order of the  $\text{TE}_0$  and  $\text{TM}_0$  modes was interchanged as compared to their expected order in an isotropic film. The measured values of refractive index agreed extremely well with a Drude model calculation based on the estimated volume fraction of each of the film constituents.

An intercomparison of techniques for measuring the thicknesses of films of  $\sim 1 \mu\text{m}$  thickness was made based on measurements reported in the literature and measurements conducted at the National Bureau of Standards. Six techniques were compared--stylus profiling, dual beam interferometry, multiple beam interferometry, prism-coupler method, ellipsometry, and channeled spectra. All of the techniques are of comparable accuracy; dual beam interferometry and stylus profiling have a conservative accuracy of 2.5 percent for  $1 \mu\text{m}$  thick films; ellipsometry, channeled spectra, and the prism-coupler method are accurate to about 1 percent; multiple beam interferometry is accurate to about 0.5 percent. The stylus instrument and the dual and multiple beam interferometry require an opaque, reflecting specimen; the prism-coupler method, ellipsometry, and channeled spectra require transparent specimens; stylus profiling and the prism-coupler require contact with the specimen.

At the present time we are designing and constructing apparatus to measure optical scattering due to micro-irregularities in thin films. Two systems are to be built; a total integrated scattering (TIS) apparatus to measure all the radiation scattered back within a  $2\pi$  hemisphere, excluding radiation within  $3^\circ$  of the normal; an angular scanning apparatus to measure scattered radiation in the equatorial plane as a function of



the scattering angle. The TIS will allow for rapid intercomparison of specimens prepared under various deposition conditions. The angular scanning apparatus will provide information about the dimensional scale of the micro-irregularities in the film; the smaller the scale of the irregularities, the larger the scatter at large scattering angles.

#### Standard Reference Materials for the Glass Industry Subtask 2 of Task 12154

M. J. Cellarosi, D. J. Cronin, and W. K. Haller

#### Dielectric Constant SRM

Activities leading to the certification of a dielectric constant glass standard have been completed. This work involved the completion of interlaboratory comparisons with industrial laboratories, statistical analysis of data, test methods and procedure improvements, sample preparation for SRM packaging, and issuance of SRM certificate and related publicity literature.

This project was undertaken at the request of ASTM Committee C14.04 on Physical and Mechanical Properties of Glass principally to resolve serious measurement discrepancies for the glass dielectric constant that existed in industry. SRM 774 for the dielectric constant and related loss characteristics now issued for sale by NBS will primarily support the expanding role of glass in electrical/electronic applications. Such applications include: envelopes for devices, substrates, encapsulation, windows for electromagnetic waves, capacitors, insulation, etc. The SRM will also help in energy conservation efforts (e.g., low loss insulators and dielectrics), and in the evaluation of glass and other material properties, such as dielectric breakdown, moisture content, deterioration, etc. The standard is also expected to be of interest to the plastics industry as the inherent long-term stability of glass is superior to that of plastics for calibration purposes.

#### Glass High-Temperature Resistivity SRM

This project is listed as one of the priorities by the ASTM C14 Committee on Glass SRM development.

Glass resistivities as a function of temperature in the molten range are important parameters for effective utilization of electrical power, for increased productivity, higher glass quality, and in reduction of air pollution from glass furnaces. Glass resistivity is also a very important factor in the design of melting process equipment and this SRM will be of benefit to the glass industry as an increasing number of melting operations are converted to electrical power.

Procedures and samples (SRM 711, Viscosity Standard) were distributed to the participating industrial laboratories. A second round-robin now in progress utilizes procedures employed in high temperature viscometry. These procedures enable the generation of simultaneous resistivity/viscosity data. Viscosity SRMs provide the necessary temperature calibrations.

A new measuring bridge was purchased, and other instruments and equipment in the Division and elsewhere at NBS were evaluated for possible use. Calibrations and equipment modifications are in progress. Standard KCl aqueous solutions are used in the calibrations and for the determinations of the cell constant required for the calculation of resistivity.

It is important to note that SRM 711 glass is already certified for electrical resistivity in the lower temperature range, and for dielectric constant and associated ac loss characteristics. Therefore, SRM 711, when it is certified for resistivity in the molten range will cover a broad spectrum of electrical properties.

#### Viscosity SRM

In anticipation of replacing viscosity SRM 710 (soda-lime-silica glass) a new high temperature viscometer is being constructed for use in the certification process. The viscometer utilizes a commercially available torque measurement system and a furnace designed at NBS. To simplify operation of the instrument a new torque meter was obtained that will allow driving the inner cylinder and measuring the resultant torque. Previously, it was necessary to rotate the crucible which presented a number of experimental difficulties. With the new torque meter these difficulties can be eliminated. Furnace construction and refinement of mechanical details will be carried out to allow ample time for calibration prior to SRM certification.

#### Other SRM Development Activities for the Glass Industry

In cooperation with ASTM Committee C14.91 on Standard Reference Materials, and a glass industry supported part-time research associate, NBS is involved in developing a series of six glass SRMs which had been established as priorities by industry. An update on the progress and status of these candidate SRMs follows.

#### Thermal Expansion Standard with a Coefficient Approximately $90 \times 10^{-7}/^{\circ}\text{C}$

Soda-lime glass rods (Kimble R-6) were made by the Kimble Division of Owens-Illinois and received at NBS. Glass homogeneity as determined by interlab testing is excellent. However, preliminary expansion measurements show that the expansion coefficient is sensitive to thermal history below 300 °C. This effect may rule out R-6 as an SRM. Other compositions are being considered.

#### Glass with a Well-characterized Ferrous/Ferric Ratio for an Analytical Standard

A draft of a wet-chemical consensus method for the determination of ferrous iron was developed. Interlab testing is in progress using an amber soda-lime and a borosilicate glass to determine the ferrous/ferric ratio by difference between iron in the ferrous state and total iron. NBS SRMs 620, 621, 1830, and 1831 are also being used to aid in establishing an ASTM Test Method.



### Soft Borosilicate Glass for an Analytical Standard

A glass composition supplied by Johns-Manville was processed by Corning. Approximately 4800 wafers made by the Corning Clearform process were received at NBS. Interlaboratory x-ray fluorescence chemical homogeneity evaluations are in progress.

### High Alumina Sand for an Analytical Standard

A candidate sand was prepared by grinding a high alumina sand to 98 percent minus 200 mesh. This flour was magnetically separated at Owens-Corning to remove iron. Evaluations of this material, however, proved that the material was not acceptable and was therefore rejected. Feldspar and silica flour were blended, but even this formulation had to be rejected because it had a too broad particle size range. High alumina sand, provided by Santa Cruz Aggregates Company, was ground by Ferro Corporation and shipped to NBS. Interlaboratory testing is in progress to analyze chemical homogeneity and suitability as candidate SRM.

### Multicomponent Glass for Analytical Standard

This glass is being prepared by Corning, and it will be formed in the same manner as indicated for the borosilicate glass above, after the Clearform method is proven to be sound.

### Fused Quartz Annealing Point SRM

The quartz product business is an expanding activity as new uses for quartz are developed. Quartz performance is highly dependent on the chemical and physical properties of the material. One of the critical properties is viscosity. New developing applications of quartz include the semiconductor crucible business, and fiber optics technology. This SRM has been proposed by ASTM Subcommittee C14.04 on Physical and Mechanical Properties of Glass as a logical extension to other NBS standards for viscosity. Quartz rods made by General Electric have been distributed by NBS to establish the homogeneity of the material for a fused quartz annealing and strain point SRM.

### Density SRMs

Density is a very important property for quality control in glass production. Eight industrial laboratories have indicated a strong interest in establishing glass density SRMs. ASTM Committee C14.04 on Physical and Mechanical Properties of Glass has requested that NBS certify the density of some existing SRMs. Three glasses were identified as likely candidates: viscosity SRMs 711 and 717 and liquidus SRM 773.

### Glass Standard Reference Materials Liaison

The Glass Group maintains broad relations with industry, research and development organizations, and academia concerning the scientific and technological progress in glass and related products. Active participation is extended to various standards and measurement bodies. Glass Group personnel hold offices in the International Commission on Glass and ASTM Committee C14 on Glass and Glass Products.



## Resource Recovery and Utilization

This project has been pursued in response to the Resource Conservation and Recovery Act of 1976. In this Act, NBS is directed to provide guidelines for the development of specifications and related standardization for materials recovered from waste. NBS work and funding up to this fiscal year have been coordinated through the Office of Recycled Materials and will be terminated this year.

One major benefit for recycling glass is energy savings. Other benefits are extension of furnace life linings and plant emission control. Activities involved the characterization of recovered glass at various reclamation facilities, large-scale production runs, plus the development of specifications and test methods applicable to glass recycling in fiber glass production. NBS has cooperated with ASTM Committee E38 on Resource Recovery, the glass industry, reclamation facilities, and other organizations, principally in activities on specifications, test methods, and interlaboratory comparisons.

Cooperative testing activities by NBS, the National Center for Resource Recovery, Owens-Illinois, and EG&G were carried out for glass recovered as the Recovery I reclamation facility in New Orleans, LA. Laboratory results covering refractory and magnetic/non-magnetic contaminations, organic contamination, particle size, melt evaluations, and viscosity are used as inputs in preparing for a large-scale production at a glass container plant in Atlanta, GA. The correlation of lab data with the actual production output will be used to design second generation glass recovery plants.

### Glass SRMs for Other Industries Subtask 3 of Task 12154

D. H. Blackburn, D. J. Cronin, and D. A. Kauffman

### Glass Standards for Small Particle Chemical Analysis

Glass has many properties which make it uniquely suitable for analytical standards in microbeam analysis. Numerous very different oxide glass-forming systems give a variety of matrices to select from in order to minimize interfering and overlapping responses which can confuse interpretation of analytical data; furthermore, there is an overall matrix effect which can now be evaluated and interpreted. As an example, instrument responses will be quite different for a given element when it is incorporated in a  $\text{TeO}_2$ -BaO matrix or in a  $\text{B}_2\text{O}_3$ -Li<sub>2</sub>O matrix.

Other desirable features of glass for this application are excellent physical and chemical stability, lack of structure, and the fact that glass can be made extremely homogeneous even with a large number of elements present. Furthermore, one of the most useful features is that glass can be fabricated into a variety of shapes and sizes from the same parent glass melt of known composition. Bulk specimens can be fabricated by conventional grinding techniques, continuous fibers can be formed in kilometer lengths with diameters as small as 3 micrometers, spheres

ranging in size from 100 micrometers to submicrometer diameters, and thin films below 2000 Å in thickness can be produced.

A major effort during FY82 was the construction of a facility for the preparation of glasses containing the radioactive elements uranium and thorium. This will enable the Glass Group to produce glass melts and prepare micrometer and submicrometer spheres of radioactive glass in a safe environment. The facility is near completion and will be in operation before the end of FY82. Work has continued on the production of glass standards of various compositions for the Center for Analytical Chemistry. A new Standard Reference Material for Microprobe Analysis is in the process of being certified. This standard, SRM 471, will consist of 15 glasses and is an expansion and upgrading of Research Material No. 30. It will consist of five glasses in the systems  $\text{PbO-SiO}_2$ ,  $\text{GeO}_2\text{-PbO}$ ,  $\text{P}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-MgO}$ ,  $\text{SiO}_2\text{-BaO-ZnO}$ , and  $\text{B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Li}_2\text{O}$  giving very different matrices. Five other glasses with the same matrices but doped with Al, B, Zr, Ti, Ce, Ta, Fe, and Li and another series doped with Zr, Ti, Ni, Eu, Mg, Ba, P, Ge, U, Th, and Cr. The compositions were carefully chosen for microprobe use to give a maximum amount of analytical standards information.

#### Analytical Standards for Biological Materials

Further progress has been made in extending the use of glass analytical standards to the analysis of biological materials. This work is a cooperative effort in conjunction with groups at the National Institutes of Health. A lithium borate glass matrix was selected for the work since it is necessary that the matrix have a low Z similar to animal tissue. Elements such as K, Ca, S, I, F, N, and Hg have been incorporated into various lithium borate matrices. Results are being published in the Journal of Microscopy in a paper entitled Low Z Glass Standards for Biological X-ray Microanalysis, by C. E. Fiori and D. H. Blackburn. Other work was presented at the 17th Annual Conference of the Microbeam Analysis Society, August 1982, in Washington, DC. A paper is in preparation entitled Energy Dispersive X-ray Microanalysis of Biological Specimens by M. C. Foster, W. A. Hagins, and D. H. Blackburn, and is to be submitted to the Journal of Analytical Chemistry.

#### Microspectrofluorometric Standards

Expanding use of fluorescence in immunochemical and cytological analysis as well as particulate analysis has made development of microfluorescence standards of increasing importance. A series of stable luminescent microspheres was developed using a silicate matrix glass doped and codoped with europium and terbium. Microspheres formed from these glasses were in the size range of 5 to 50  $\mu\text{m}$  in diameter. This work was presented at the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, March 1982, at Atlantic City, NJ. A more detailed presentation will be published in the Journal of Analytical Chemistry entitled Inorganic Ion Doped Glass Spheres as Microspectrofluorometric Standards by R. A. Velapoldi, D. K. Hancock, J. R. DeVoe, and D. H. Blackburn.



## Nuclear Waste Leachability Research Material

Though the NBS Nuclear Waste Program was discontinued at the start of FY82, contact has been maintained with the nuclear waste community, particularly with regard to the need for standards. A leachability study was carried out in conjunction with H. M. Kingston and M. S. Epstein of the Center for Analytical Chemistry. The purpose of the test was two-fold: one purpose was to investigate the effect of composition variation on leaching behavior of the glass composition which had been proposed as a research material; the second purpose was to tighten MCC-1 test procedures to improve the quality of data obtained. The results of this test were successful on both counts. The leach results for replicates of the same glass showed uncertainties that were approximately equal to the uncertainty of the analysis for a given element.

The high quality analytical results allowed a maximum amount of information to be obtained concerning composition variations. This showed that increasing Na, B, Cs, and Mo decrease the glass durability, while Ti, Sr, Nd, and Ce improve the glass durability.

The results of this study were reported at the Materials Characterization Center Workshop on Leaching Mechanisms held at Gaithersburg, MD, May 19-21, 1982.

### Special Glass Developments Subtask 4 of Task 12154

D. H. Blackburn, D. J. Cronin, A. Feldman, L. H. Grabner, W. K. Haller, D. A. Kauffman, and R. M. Waxler

### Laser Glasses

Collaboration of the Glass Group with the Lawrence Livermore Laboratory (LLL) has continued and expanded in scope. Over 100 different glass compositions were prepared of various compositions in silicate, phosphate, and borate systems, and doped or codoped with rare earth transition metal oxides. These glasses are used in the LLL continuing investigation of glass laser systems. In addition to the ongoing work, a new project was started in mid-year. This involves developing a borate laser glass in which Yb is the active species. Earlier studies showed that Yb in a borate glass matrix may be suitable as a laser system.

This project involves three phases. The first phase is to produce a series of simple binary glasses containing Yb to investigate the effect of the different modifying ions on the various optical properties of interest. These include glasses of alkali and alkaline earth borates in addition to borates of Al, Y, and La. These glasses have been delivered to LLL for optical property measurements.

The second phase of the project involves the investigation of the effect of water on fluorescence behavior of Yb. Other work has shown that the presence of water in the glass adversely affects the fluorescence behavior of Yb. This portion of the project involves preparing a series of glasses varying the water content to obtain quantitative information on



this effect. To accomplish this it is necessary to develop a direct technique to determine water content in borate glasses. This work is currently underway.

Once the composition effects have been determined for the individual modifier ions the third phase involves development of a glass composition that maximizes laser properties and can be made in large pieces of optical quality. This involves trade-offs in optical properties, chemical durability, and glass-forming ability.

### Glasses for Fiber Optic Sensors

At present there is considerable interest in the use of fiber optics for sensors of physical parameters, such as temperature, pressure, electric fields, and magnetic fields. The Navy has a particular interest in developing acoustic sensors. The Naval Research Laboratory (NRL) has therefore requested that NBS aid in the development of glasses for fiber optic sensor materials and the characterization of these glasses as to elastic moduli, thermal expansion, thermo-optic constant, and photoelastic constants.

The fiber-optic sensor system is conceived as being composed of two parts: the sensor itself which is located a long distance from a monitoring station, and fiber optic leads that connect the sensor to the monitoring station. The emphasis of our program is on materials to produce fiber-optic leads that are insensitive to pressure and temperature fluctuations. The fiber optic leads are to pass through regions of the ocean that are subject to such fluctuations. It is important that the optic path of propagation in the fiber core be immunized against these fluctuations in order to minimize optical noise in the sensor system.

At present, the main emphasis of the program is to produce cladding glasses that lower the pressure sensitivity of the core. Work at NRL has shown that a cladding material with a high Young's modulus acts to minimize the effects of pressure on the fiber core. We have now produced a total of 19 glasses whose Young's moduli exceed the target value of  $9.5 \times 10^{10} \text{ N/m}^2$ . Furthermore, we have measured the linear thermal expansion coefficients of these glasses and have found some to have very small values ( $\alpha < 3 \times 10^{-6}/\text{K}$  at  $20^\circ \text{C}$ ). This result is highly desirable because when claddings of these materials are fused to core materials, made predominantly of fused silica, stresses due to differential thermal contraction will be minimized, thus increasing the probability of successfully drawing a pressure insensitive fiber. At present we are preparing a cylinder of cladding material made from one of the glasses we have produced which is to be used in a test drawing of a pressure insensitive fiber at a commercial vendor.

In addressing the second problem, the temperature insensitive fiber, work at NRL has shown that temperature insensitive fibers would have a core with a small thermo-optic coefficient at constant density  $(\partial n / \partial T)_p$ . We have conducted a literature search which suggests that  $(\partial n / \partial T)_p$  would be small in borate glasses, phosphate glasses, and glasses with a high

fluoride ion content. In addition, we have determined  $(\partial n / \partial T)_p$  for three commercial athermal glasses but have found the values in all the glasses to be rather high.

#### Fluorescence Standards for the U.S. Post Office

Two glass development programs are currently underway for the U.S. Postal Service. Both involve producing fluorescent glasses to be used as standards for the calibration of automatic letter cancelling equipment.

The first project involves development of a material showing high intensity red fluorescence for use with existing equipment. Eu ions are used as the active material. To obtain the required intensity it was necessary to incorporate the Eu in a  $Y_2O_3$  matrix. To obtain the finished product the Eu-doped  $Y_2O_3$  powder is mixed with fine glass powder, pressed, and sintered. This provides a dense material giving a smooth surface finish that can be easily cleaned and the fluorescent intensity can be accurately controlled by the amount of Eu-doped  $Y_2O_3$  incorporated in the glass matrix.

The second project calls for development of four different materials to be used in a new calibration device under development at USPS. The materials required are a green phosphor, red phosphor, red fluorescent, and one material showing no fluorescence. The intensity levels required are such that the first three materials can be produced directly from glass melts.

#### Preparation and Characterization of Thin Films

##### Subtask 5 of Task 12154

E. N. Farabaugh, J. L. Fink, D. M. Sanders, M. E. Wilke, S. A. Hurwitz, K. M. Summers, and A. Tegtmeyer

The facility for the production and characterization of thin films by coevaporation has been operated during the past year in four research areas: glass formation in multi-component thin films, chemical reactions which may lead to stress corrosion in ceramics, protective films on metals, and thin film mechanical properties.

To carry out these studies, it has been necessary to enhance the capabilities of all of the subsystems of the facility. Simultaneous with the system improvement, we have carried out preliminary experiments in each research area. These have established experimental feasibility, and determined the direction of future experimental work. The results of some of this work have been published.

#### System Improvement

The primary system modifications last year involved the carousel-loadlock chamber and the surface analysis chamber. In addition to establishing a base pressure in the loadlock of better than  $1 \times 10^{-9}$  mbar using a combination of a liquid nitrogen trap and bakeout to 250 °C, we installed



the capability of heating substrates in the loadlock using quartz lamps to temperatures in excess of 600 °C. This modification should permit us to anneal thin films deposited at pressures of  $1 \times 10^{-8}$  mbar in still better vacuums to attempt to dislodge adsorbed water and other impurities. It is our hope that such a treatment will produce films having a pristine chemical structure for subsequent stress-induced reaction studies.

The computer software for the automation of the surface analysis system has now been installed. In order to permit the use of the Hewlett-Packard System HP-1000 minicomputer for other applications, it was necessary to generate the software purchased from the supplier into a custom designed operating system. In addition, a data acquisition interface to monitor and control all aspects of the deposition process including residual gas pressures, individual deposition rates, and deposition substrate temperatures has been delivered. In the next year, we will connect the interface to the deposition hardware and monitoring equipment and write computer programs to permit the computer to store all process parameters for every thin film produced. This system will also provide computer-driven control signals to permit gradient index mixed oxide films to be deposited.

During the year, an electron flood gun for charge compensation during ESCA and ion scattering spectroscopy (ISS) measurements was installed. A device for in situ deposition of a gold spot on any substrate for absolute electron energy calibration was designed, constructed, and mounted between the loadlock and the surface analysis chamber. When used together, the electron flood gun and the gold spot evaporation capability permit accurate determination of binding energies of dielectric samples.

Finally, we acquired and installed a dual anode x-ray source for the ESCA system. This will allow us to quickly distinguish between photoelectron peaks and Auger peaks excited by the x-ray irradiation.

#### Noncrystalline Optical Coatings

This work has been discussed above under "Physics and Chemistry of Glass" and "Optical Properties of Materials."

#### Fracture Studies

In order to understand the role of the gaseous environment upon the reactions leading to stress-induced failure in ceramic materials, it is first necessary to understand the nature of the chemical reactions which can take place at freshly produced surfaces having stress-dependent reaction rates. Freshly produced fracture surfaces are a reasonable model for the material which is immediately in front of an advancing critical flaw. This work is being carried out with the Fracture and Deformation Division (562).

To meet the above objective, short rod specimens of  $\text{SiO}_2$ ,  $\text{MgF}_2$ , and soda-lime-silica glass were prepared. These specimens were subsequently fractured in the loadlock under vacuums of  $1 \times 10^{-9}$  mbar. The freshly fractured surfaces were then characterized using both angle resolved ESCA and normal take-off angle ESCA with computer controlled data collection and subsequent peak analysis. Finally, the resulting fresh fracture



surfaces were exposed to air and water vapor prior to a second ESCA analysis. From the resulting ESCA spectra of the  $O_{1s}$  and  $O$  Auger peaks, oxygen bonded to silicon atoms can be distinguished from oxygen bonded to hydrogen atoms. The differences are, however, subtle and will require the calculation of the peak's second derivative to permit stress-dependent reaction rate studies. A small program to make such calculations will be written shortly.

In the fracture of  $MgF_2$ , we observed both oxygen and carbon ESCA peaks using the angle resolved (surface sensitive) mode even at nominal vacuums of  $1 \times 10^{-9}$  mbar. Since monolayer coverage requires one hour with unit sticking coefficient at this vacuum, it is speculated that the observed peaks resulted from adsorption of  $CO_2$  or other gases from contamination. This contamination may stem from gases released from the bulk material in the fracture process. For this reason, the  $MgF_2$  experiments will be repeated using a liquid  $N_2$  cooling coil which has been installed in the loadlock chamber. In either case, the observed  $O$  and  $C$  peaks were substantially diminished when the fresh  $MgF_2$  fracture surface was allowed to remain in the surface analysis chamber at  $1 \times 10^{-11}$  mbar vacuum overnight. This implies a physical adsorption mechanism.

In the last series of vacuum fracture experiments, ammonia was introduced into the loadlock in an attempt to observe a  $N_{1s}$  ESCA peak in the angle resolved mode. Ammonia was chosen because experiments had indicated that this reactant causes slow crack growth in  $SiO_2$ . In addition, it was speculated that its reaction with the  $SiO_2$  surface could be monitored if the  $N_{1s}$  ESCA peak could be observed. Since  $N_2$  is not normally adsorbed on ceramic surfaces under UHV conditions, the  $N_{1s}$  ESCA peak constitutes a new peak for monitoring stress-dependent reaction rates. Because it is an entirely new peak rather than a shoulder on an existing peak as in the oxygen Auger case, such an approach provides distinct analytical advantages for monitoring changes in reaction rates with stress. In addition, this reactant should not require such stringent vacuums as are necessary in monitoring changes in the oxygen Auger shoulder associated with hydroxyl oxygen.

In the first series of experiments with ammonia it was discovered that the  $N_{1s}$  peak could be observed in angle resolved ESCA if signal averaging is employed. In order to produce high quality spectra it was necessary to scan over this one peak for times in excess of 15 minutes with existing equipment. The computer, therefore, proved to be extremely useful for this measurement.

Ammonia reactions have been observed so far on both  $SiO_2$  fracture surfaces and freshly deposited  $SiO_2$  thin films. Preliminary measurements of these reactions on  $SiO_2$  films stressed in tension by substrate bending show an apparent increase in  $N_{1s}$  peak size when compared with unstressed films subjected to equivalent ammonia exposure.

In the next year we will seek quantitative confirmation of the above-reported effects and extend the fracture experiments to other gaseous environments.

This work is being carried out with the Fracture and Deformation Division.

### Mechanical Properties of Thin Films

Studies of high temperature viscous deformation commonly known as creep have been carried out for many years on bulk materials. Such studies have not been made in thin films because of the experimental difficulties involved. This is unfortunate because such information could lead to improved protective coatings for metal parts used in high temperature corrosive environments such as turbine blades. In addition, the effect of thickness on creep in ceramic materials might improve the understanding of bulk creep theories. For these reasons, the development of the capability which will ultimately permit such measurements is necessary.

Central to being able to make such measurements is the ability to produce well-defined thin ceramic films which can be separated from a portion of their substrates over as large an area as possible. This is necessary in order to permit the measurement of thin film mechanical properties independent of the influence of that substrate.

To achieve this goal several approaches have been attempted. One involves the deposition of the films on substrates which can be dissolved in an appropriate solvent. Examples of substrate-solvent combinations are glass/ five percent HF solution and sodium chloride/water. The inherent problem with this technique is the difficulty to remove the released films from the solvent without damage. This difficulty is also found with thin film release agents used to cause the separation of the film from its substrate.

Recently, we have been investigating the possibility of adapting halogen transport of metal substrates as an alternative method of producing unsupported films. This technique, which is normally used to refine metals such as zirconium, involves the reaction of the metal at a lower temperature to form a volatile iodide which dissociates at a filament heated to a higher temperature. The zirconium is deposited on the filament and the iodine released to react with more substrate material. Such a technique does not involve the liquid state and may permit the production of very thin unsupported films.

Finally, we have ordered a microhardness tester for use in a scanning electron microscope. This tester will be used to explore the influence of thin film microstructure on hardness.

### Protective Films on Metals

The corrosion-hardness of many metals is the result of the formation of protective oxide films. In spite of this technological importance the exact structural character of such films is still poorly understood. One theory suggests that the amorphous character of such films with resulting lack of grain boundaries is the most important prerequisite for corrosion protection. Earlier studies of films produced on iron alloys with differing chromium contents showed a greater disorder in passive films on metals with greater chromium concentrations. These films were in turn the most protective of the underlying metal.

In preparation for studies of such passive films, we have been exploring the use of the ESCA technique for the quantitative analysis of films which have been produced on stainless steel using electrochemical passivation techniques. We have been carrying out qualitative analysis of the ratio of iron to chromium as a function of film depth for several different passivation conditions. The same films are being characterized using ellipsometry to provide an in situ monitor of the passive film growth.

We expect that the results of the study will provide the necessary background for a characterization of the structure of model passive films produced by codeposition.

This work is being carried out in conjunction with the Corrosion Group.



CERAMIC PROCESSING AND DURABILITY SCIENCE  
Task 12156

Task objectives focus on the development of theory, measurement methodology, standards, and data for producers and users of technical and bulk ceramics. Polymers, glasses, and metals also are researched when specialized data and measurements techniques necessary for this task require further refinement for application to ceramic systems. Emphasis is placed on scientific aspects of the powder-process-structure-property linkage that influence performance, reliability, and chemical/physical durability.

Research in this task includes significant collaboration with other tasks in this Division and with other Divisions at NBS. Considerable aid and expertise are given by the JCPDS Research Associateship (staff of seven), one ceramic engineer guest worker from private industry, two ceramic engineering co-op students, one postdoctoral appointee shared with another task, and two guest workers from the U.S. Army. In addition, R. Snyder, Alfred University; A. E. Evans, University of California/Berkeley; R. Coble, Massachusetts Institute of Technology; and D. Readey, Ohio State; rendered valuable consultation during this year. Partial funding has been provided by various divisions in DOE, DOD, NASA (through NBS subcontracts), Solar Users Association, U.S. Postal Service, and several offices (OSRM, ORM, and ONDE) at NBS. Many new contacts are being established for the purpose of assessing industrial needs in ceramics research to help fashion the NBS role in future programs. The user community established via cooperative programs, professional societies and committees, as well as via the dissemination of research results through publications, SRM development, reports, etc., presently includes numerous industrial, academic, and Government interests. Major research activities are summarized by the following subtask areas:

1. measurements, standards, and processing applicable to ceramic powders and particulates;
2. physical/chemical properties and durability of ceramics;
3. structural chemistry of materials at elevated pressure and moderate temperature; and
4. evaluation and compilation of data.

Subtask 1 is concerned primarily with quantitative x-ray diffraction (XRD) techniques, standards, and characterization data for powdered materials, as well as for consolidated and densified or reacted products. This research also serves as input for the Joint Committee for Powder Diffraction Standards (JCPDS) Research Associateship established at NBS (Subtask 4). A major accomplishment this year has been the development of x-ray line profile models which, together with application of digital data collection, has improved the accuracy of x-ray powder data measurements by a factor of three to five.

Subtask 2 emphasis is on chemical/physical properties, durability, and microstructural characterization of materials, including structural and

electronic ceramics, such as silicon carbide, zirconia-based ceramics, and  $\text{YCrO}_3$ . The latter has been shown to be an ideal model material for the study of microflaws in ceramics by elasticity and small-angle neutron scattering (SANS) measurements.

In Subtask 3, the structural chemistry of a wide variety of materials is under investigation at elevated pressure using the diamond anvil pressure cell (DAPC) facility and associated analytical techniques. A program was initiated to investigate high pressure--moderate temperature phase transitions for doped zirconia materials using the DAPC. In addition, the structures of amorphous materials were determined at elevated pressure for the first time using radial distribution function (RDF) analysis and the DAPC.

The Materials Performance Data Center and collaborative efforts with the JCPDS are included in Subtask 4. NBS Monograph 25--Section 19 is scheduled for publication this fall, and the handbook, Construction Materials for Coal Conversion--Performance and Properties Data (600 to 700 pages) is now under review for publication in 1982.

Activities within each subtask are detailed below.

#### Ceramic Powders and Particulates--Measurements, Standards, and Processing Subtask 1 of Task 12156

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<sup>1</sup>Guest Worker from Trans-Tech, Inc.

#### SRMs for X-ray Diffraction (XRD) Analysis of Powders

Two instrument 2 $\theta$  calibration standards have been certified: SRM 640a silicon powder and SRM 675 fluorophlogopite (FP) powder. The former is a replacement for SRM 640 which was out of stock (> 850 units sold). SRM 675 fluorophlogopite is intended as a low 2 $\theta$ /large d-spacing standard. In reflection geometry, only the 00 $\ell$  lines are observed, and this simplifies the pattern for use as an internal standard. The d-spacing of the 001 line is 9.98104 (12) Å (2 $\theta$  ~ 8.8° for  $\text{CuK}\alpha$ ).

The certification methods employed were quite similar and involved use of profile fitting to accurately determine peak position. The profile function is a rational polynomial,

$$f(x) = \frac{1}{1 + A_1 X^2 + A_2 X^4} ,$$

where  $A_1$  and  $A_2$  must be positive or zero, and  $X = 0$  at the peak. Asymmetry was introduced by separately refining the parameters  $A_1$  and  $A_2$  above and below the peak. The  $\text{CuK}\alpha_2$  profile was assumed to be identical in shape with the  $\text{CuK}\alpha_1$  profile. The model contains seven parameters:  $2\theta_p$ ,  $I\alpha_1$ ,  $I\alpha_2$ ,  $A_1^l$ ,  $A_2^l$ ,  $A_1^h$ , and  $A_2^h$ . The background was determined from data points far removed from the peak and was not refined. The agreement factor,



$$R = \left\{ \frac{\sum_i (I_{\text{calc}} - I_{\text{obs}})^2}{\sum I_{\text{obs}}^2} \right\}^{1/2},$$

for silicon profiles typically was 0.02 to 0.04.

The silicon lattice parameter was determined using silver and tungsten internal standards. The fluorophlogopite d(001) was determined using silicon SRM 640a and tungsten internal standards. In both cases, a smooth polynomial was fit to the peak positions of the internal standard lines. The rms deviation from the polynomial curve was usually  $0.003^\circ 2\theta$  or smaller. Least squares refinement of  $a(\text{Si})$  or  $d_{001}$  for FP gave rms deviations of similar magnitude. Both SRMs were proven to be homogeneous through multiple measurements ( $> 20$  in each case).

The application of digital data collection and profile refinement was a major accomplishment of this year. The accuracy in  $2\theta$  measurement was demonstrated to be  $\approx 0.03^\circ 2\theta$ . This value is three to five times better than the average error obtained by our strip chart recording/measuring methods. The profile model employed is shown to be superior to modified Lorentzian or Pearson VII functions. A paper on this function was given at the March 1982 American Crystallographic Association (ACA) meeting and has been submitted to the Journal of Applied Crystallography for publication.

Other on-going SRM-related projects include, (1) certification of respirable quartz ( $\text{SiO}_2$ ) for relative intensities, reference intensity ratios and percent amorphous content; and (2) research on development of a submicron crystallite size SRM (see below). Dr. R. McKenzie, Analytical Chemistry, is testing the quartz for homogeneous particle size distribution. Upon completion, the XRD measurements will be made. Development of quantitative methods to determine glass or amorphous content is expected to have significant impact on the analysis of  $\text{SiC}$  and  $\text{Si}_3\text{N}_4$ -based structural ceramics and powders, as well as of more conventional bulk refractories for metal processing. In conjunction with this work, research on preparation of a cristobalite SRM will begin next year.

#### Preparation of Submicron Crystallite Powders

Research is being conducted to develop a submicron crystallite size SRM to calibrate x-ray line-broadening measurements critical in establishing baseline conditions for crystallite size, strain, and compositional variation determinations. Methods of preparing magnesium oxide powders consisting of submicron crystallites are being developed. Two methods are under study: (1) production of  $\text{MgO}$  "smoke"; and (2) calcination of a magnesium containing precursor. An apparatus to burn magnesium metal and to electrostatically collect the smoke was built and operated to produce the particles. The smoke particles have a cubic morphology, so an independent determination of particle size can be made by electron microscopy. The second method, using the decomposition of basic magnesium carbonate, has been initiated. Conditions are being sought in this latter method which will yield crystallites which can be geometrically sized, as well as sized by x-ray line-broadening measurements.



## Characterization of Particulates, Residues, and Corrosion Products

### Physical and Chemical Characterization of Fossil Fuel Residues

This program relies heavily on the practical application of advanced XRD techniques and microstructural/microchemical methods as developed by this group and on other analytical methods available at NBS.

During the year, selection of methods of analysis, development of new methods and their application to test or simulated samples of ash residues were carried out for a DOE supported program. Methods and instrumentation chosen include: scanning electron microscopy with energy dispersive x-ray analysis (semi-quantitative); image analysis (quantitative); Auger methods for surface analysis (semi-quantitative); and x-ray powder diffractometry (both qualitative and quantitative). A spray dryer constructed to prepare samples with a minimum of crystallite orientation for x-ray analysis was tested successfully, and used to prepare reference samples (fig. 1) for quantitative analysis. Application of the computer programs of C. R. Hubbard, NBS and R. Snyder, Alfred University (see below), for quantitative XRD show the method is quite promising.

Samples of ash residues for analysis were received during April and May of 1982, after an unanticipated delay. Analysis of the samples is now in progress. In addition, nine ash samples were characterized at the request of DOE as a measure of their sampling protocol.

Three collaborative studies of ash residues from emerging energy technologies were completed in FY82. They are:

- a. "X-ray Analysis of Selected R-D-F and Coal Samples as a Function of Temperature," with E. Domalski and R. Kelly, NBS Center for Thermodynamics and Molecular Science.
- b. "Characterization of Ash Residues From a Refuse-Derived Fuel/Oil Combustion Study," with F. Hasselriis, Combustion Equipment Associates, New York, NY.
- c. "Characterization of Slag and Fouling Residues From Co-combustion of Powdered Refuse-derived Fuel With Residual Oil and Comparison With Coal and R-D-F Residues," with F. Hasselriis, Combustion Equipment Associates, New York, NY.

Little information exists on the compound assemblages and their development in ash residues from emerging energy technologies, such as the burning of refuse-derived-fuels (R-D-F), the co-firing of R-D-F and coal, or R-D-F and oil. The analyses by NBS gave a qualitative and semi-quantitative picture of the crystalline phase development of four R-D-F, four coal, and three slag and fouling samples from a utility boiler co-firing powdered R-D-F with oil. X-ray diffraction traces of the powdered R-D-F showed the destruction of crystalline cellulose due to thermal and chemical processing.

The relative amounts of glass, as distinguished from quartz and other silicates, were significantly different in the various types of R-D-F tested. This information helped to explain behavior of these fuels

in boilers, especially in those situations where firing had to be severely restricted due to slagging conditions. As R-D-F ash temperatures are raised, shifts in chemical composition were noted in the analyses. Most of the silicates became fluxed by the glass at the final temperatures representing furnace conditions.

The sulfur and iron in the oil and R-D-F reacted with calcium in the refuse, forming calcium and iron sulfates, thus reducing stack emissions of sulfur oxides. Magnesium-rich compounds were predominant in the fouling deposits formed during combustion of R-D-F, resulting from the MgO additive to the oil.

Three feasibility studies related to the effects of acid rain have been initiated for the National Park Service with J. Kruger, NBS Materials Chemistry Division.

A preliminary study of the deterioration of selected Egyptian marble and sandstone antiquities has been initiated, in part, at the request of the Smithsonian Institution with W. P. Iverson, NBS Materials Chemistry Division.

#### Computer Programs for XRD Analyses

The system of programs for determination of peak position and intensity was discussed above. Plans are to add profile refinement algorithms based on the programs developed for SRM certification this fall. Documentation of the package is also planned.

The quantitative analysis set of programs NBS\*QUANT82 have been entirely written in FORTRAN 77 by Dr. R. Snyder and C. R. Hubbard to enhance portability. Documentation has been written and example runs are being completed. Together, they will be published as an internal report along with the source code listings. Seimens Corp. intends to implement these programs on their commercial diffractometer once publically available.

The program package implements the spiking, intensity ratio, and internal standard method of XRD quantitative analysis. The latter method permits line overlap and the inclusion of elemental chemistry data to the constrained least squares phase analysis. The programs link directly with our data collection program AUTO and permit relative intensity and reference intensity ratio measurements. All programs permit use of multiple lines, multiple mounting, and multiple runs to enable assessment of the presence or absence of systematic errors. To assist the user in interpretation of the results, expected counting statistic errors are propagated and rms deviations are calculated.

Use of the programs at NBS and at Alfred University has revealed weaknesses of methods commonly employed. In particular, microabsorption and incorrect background assessment have been shown to be more serious systematic errors than commonly held. These programs will be the basis of data analysis for quantitative XRD SRMs, such as respirable quartz.



## Ceramic Oxide Powders for Plasma Spray Coatings

In cooperation with a guest worker from private industry and with active cooperation from D. H. Harris (APS Materials, Inc., Dayton, OH), flowable powders of several high purity oxides were investigated to obtain dense, adherent arc plasma spray (APS) coatings for molybdenum and mild steel substrates. Present research has focused on powders of solid solutions,  $(Al_{1-x}Cr_x)_2O_3$ , ( $X = 0.07, 0.20$ ). Conventional pure alumina APS coatings consist of metastable  $Al_2O_3$  variants (e.g.,  $\gamma$ -alumina) that undergo large volume changes during transformation to the stable  $\alpha$ -form at elevated temperatures ( $> 1000^\circ C$ ) after deposition. Pure chromia powders yield poor APS deposition efficiency due to the high vapor pressure of chrome oxide(s). Solid solution with alumina precludes this problem. However, it has also been found that chromia influences the crystallization kinetics, such that APS coatings with high  $\alpha$ -content ( $> 50$  percent) are deposited. Controlling mechanisms are not well understood at present. Annealing at  $1500^\circ C$  completes the transformation of the residual metastable phase(s) to  $\alpha$  without loss of adhesion on Mo-substrates. Complete transformation to  $\alpha$  and post-deposition densification to near 95 percent of theoretical also were accomplished by hot isostatic pressing (HIP) and  $1100^\circ C$ , 30,000 psi.

G. W. Burns (Thermal Processes Division, NBS) is currently evaluating these coatings on Mo-tubes used as thermocouple sheaths for temperature measurements in gasification and molten iron and steel environments. Preliminary tests have demonstrated that these coatings have superior abrasion and corrosion resistance (to slag).

Materials have been processed by blending and reacting active powders of appropriate components in the solid state at temperatures  $< 1200^\circ C$ . After milling, these are spray dried to produce "soft" spherical agglomerates which, subsequently, are sintered, 1500 to  $1550^\circ C$ . Dense, spherical particulates ranging from 10 to  $250\ \mu m$  are produced.

## Ceramic Green Compacts

The microstructure of densified ceramics controls their mechanical, electrical, and chemical (e.g., corrosion resistance) properties. Performance and reliability, therefore, are sensitive to microstructural evolution and control which require two major aspects of processing prior to sintering:

- a. a reactive, deagglomerated starting powder ideally of small size ( $\sim 0.1$  to  $5\ \mu m$ ), narrow size distribution, and controlled purity or dopant content, and
- b. uniform, essentially defect-free (large pores, fissures, inclusions, density gradients, etc.) green compacts consisting of deagglomerated particulates.

Defects, including agglomerates, that exist in green compacts generally are amplified during sintering at elevated temperature (and pressure), and these result in microstructural flaws that influence performance.



Normally, NDE methods (see, for example, J. Fagenbaum, Mechanical Engineering, May 1982, p. 28, for an assessment of techniques) are used to examine and, if necessary, to reject ceramics after sintering and machining. Based on the importance of ceramic processing prior to sintering (see above), identification of flaws by NDE at the green compact stage would permit early rejection and superior product control. Unfortunately, there has been very little research activity in this field, although several potential techniques have been identified (see, for example, A. G. Evans, Technical and Scientific Assessment of the Reliability of Advanced Ceramics, Report to NBS, Divisions 561/562, 1982).

The NBS Office of Nondestructive Evaluation initiated a limited green compact program for Divisions 561 and 562 during the past year. We have focused on the processing and fabrication of green compacts containing pores ( $> 10 \mu\text{m}$ ) and pore cluster defects for examination by techniques selected by Division 562 researchers.  $\text{YCrO}_3$ -based compacts (see below) also were processed for evaluation by small angle neutron scattering (SANS). Deagglomerated alumina ( $\text{Al}_2\text{O}_3$ ) and spinel ( $\text{MgAl}_2\text{O}_4$ ) powders were compacted by isostatic pressing (10,000 psi). Pore clusters were introduced via fugitive materials (e.g., latex, starch) during compaction followed by a mild "burn-out." Green compacts fabricated to shape for a specific NDE method will be developed in future work. These also will include flaws, such as fissures (via fugitive filaments) and inclusions (via spray dried, sintered particulates).

#### ZrTiO<sub>4</sub>-Based Dielectrics

In cooperation with Dr. A. McHale and Dr. R. S. Roth (Division 561), processing of  $\text{ZrTiO}_4$ -based ceramics is under investigation. These ceramics have highly desirable dielectric properties, such as a high ( $\sim 38$ )  $\xi'$  and low dielectric loss. Furthermore, doping with  $\text{SnO}_2$  can vary and control the temperature coefficient (TC) of  $\xi'$ , which is ideal for microwave integrated circuitry. Unfortunately, the material, including  $\text{SnO}_2$ -doped variants, is difficult to densify and foreign suppliers utilize sintering aids, such as Ni, Zn-oxides. These normally degrade the electrical properties of the homogeneous material.

A. McHale and R. S. Roth are investigating  $\text{ZrO}_2$ - $\text{TiO}_2$ - $\text{SnO}_2$  reactions at elevated temperature to elucidate structural chemistry and its relevance to densification and processing. This study is evaluating various sources of  $\text{ZrO}_2$  as a reactive starting powder for processing of  $\text{ZrTiO}_4$ . The key factor in past efforts to densify  $\text{ZrTiO}_4$  appears to be the presence of  $\text{ZrO}_2$  agglomerates in starting powders, and these are carried through into the initial calcine with  $\text{TiO}_2$ . The agglomerates sinter differentially to a microstructure consisting of dense and porous regions with an overall low bulk density (fig. 2). Better control and characterization of the initial powders, therefore, are necessary.

Physical/Chemical Properties and Durability of Ceramics  
Subtask 2 of Task 12156

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Structural Ceramics

Silicon Carbide and Boron Nitride

Research on silicon carbide is concerned with identifying polytypes and impurity phases in silicon carbide ceramics and with determining the product phases and their rates of formation in reactive gas environments. The silicon carbide ceramics for study are candidate materials for high-temperature heat exchangers. The reactive gas environments include air (oxygen), SO<sub>2</sub>-containing N<sub>2</sub> and a simulated coal combustion gas. When silicon carbide is heated in air, it is well known that a silicon dioxide (cristobalite or tridymite) protective layer develops. After the silicon carbide is exposed to coal combustion gas at high temperatures, evidence has been found for a variety of detrimental reaction products.

As one part of these programs, a high-temperature x-ray diffraction furnace is being developed to study the product phases at temperatures up to 1500 °C. This furnace uses silicon carbide as the heater; either the sample itself is made conducting and serves as the heater or a second piece of conducting silicon carbide serves as the heater and sample holder. The furnace is designed (1) to minimize the volume of material heated; (2) to use materials which are compatible with the sample; and (3) to use improved ceramic thermal insulating materials.

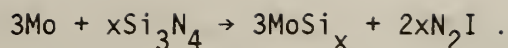
This work is supported by the Department of Energy.

The electrical conductivity of boron nitride is being measured (with H. P. R. Frederikse and W. R. Hosler) at temperatures approaching its decomposition temperature at about 2500 °C to assess the high-temperature performance of this material. Preliminary measurements to about 2200 °C indicate an activation energy of about 2.6 eV (251 kJ/mol) for the electrical conductivity. This work is supported by the Department of Defense.

Mo-Silicides.

In cooperation with the Harry Diamond Laboratories and G. W. Burns (Thermal Processes Division, NBS), chemical reactions involving Mo-Si-N were investigated at elevated temperature. Both groups are interested in coating the interior of Mo thermocouple and/or fluidic pyrometer sheaths with Mo-silicides to protect the refractory metal against oxidation at ~ 1550 °C. We developed a technique based on the following reaction:





$\text{Si}_3\text{N}_4$  submicron powder is packed into a Mo sheath. The reaction proceeds via diffusion of Si at temperatures at and above 1400 °C (in  $\text{N}_2$  10%  $\text{H}_2$ , 1 atm.) to produce a chemically graded coating consisting of  $\text{MoSi}_x$  phases (fig. 3). Kinetics of the silicide process are under investigation and a manuscript describing the process and pertinent phase relations is in preparation.

#### Microfissuring in $\text{YCrO}_3$ Ceramics

In cooperation with Dr. E. D. Case (Division 562), densified ceramics based on  $\text{YCrO}_3$  are under investigation to develop small-angle neutron scattering techniques suitable for detection and analysis of microfissures. Reactive powders of  $\text{YCrO}_3$  were obtained by calcining ( $\sim 700$  °C) a precursor prepared from  $\text{Y}_2\text{O}_3$  dissolved and reacted in ammonium dichromate solution. Green compacts (cylinders) were fabricated by isostatic pressing of spray dried powder at intervals between 2,000 and 10,000 psi. This permitted control of final bulk density after sintering within the range 75 to > 95 percent of theoretical. Compacts were sintered at 1750 °C (3 h) in forming gas ( $\text{N}_2$  10%  $\text{H}_2$ ) then cooled ( $\sim 100$  °C/h) to RT. Rectangular slabs were cut from these ceramics for elasticity and SANS measurements.

$\text{YCrO}_3$  was selected as a "model" material for these studies, as it apparently undergoes a phase transition near  $\sim 1100$  °C. This transition has not been fully characterized, although weak signals were obtained by differential thermal analysis (DTA). However, the associated volume change must be very small yet sufficient to induce microfissures. Thermal annealing above 1100 °C introduces microcracks into specimens while anneals below 1100 °C heal the fissures. The process is reversible, as demonstrated by elasticity measurements on as processed-annealed (< 1100 °C)-annealed (< 1100 °C) materials. Microcracked ceramics typically yield a Young's modulus < 140 GPa, while "healed" materials strengthen to values in excess of 200 GPa. Furthermore, the microcrack number density (N) can be varied by time versus temperature anneals without disturbing other microstructural details, such as density or grain size. SANS measurements (E. D. Case) correlate well with the elasticity data as changes in neutron scattering intensity and angular spread of the neutron beam are observed. Analysis of the SANS data suggest microfissure cross-sections in the 150 to 200 Å range (see E. D. Case, this report).

#### Noncentral Forces in Ionic Compounds

Work was recently completed on a phenomenological description of both the pairwise and multiple interactions in a complex of nearest neighbor atoms and a central atom in a rock salt-type lattice. The mathematical formulation which was developed identified many unrecognized possible noncentral force interactions for this structure. The noncentral force contributions to the lattice dynamics, elastic constants, and the force constant for the homogeneous lattice polarization were identified.



## Zirconia-Based Ceramics

### Grain-Boundary Measurements

AC impedance and microstructural investigation of a "grain-boundary" between two large grains of yttria-stabilized zirconia, which were formed as part of a skull-melt crystal growth process, indicated that the boundaries in this material are gaps bridged by islands of yttria-stabilized zirconia. Surface features on the grains give some clues as to the last stages of crystal growth. These features suggest that a thin layer of the melt was trapped between the grains and that this layer receded until it solidified into isolated islands of material between the grains.

### High Pressure Measurements

Zirconia and doped variations of zirconia show great promise as a useful and reliable ceramic material, because of its exceptional mechanical properties, its resistance to thermal corrosion, and its fast-ion electrical properties. The material also has the ability to be toughened by controlled composition and particle size of the tetragonal and cubic phases. Crack propagation can be halted by the martensitic tetragonal-monoclinic transition or by second phase dispersions in monolithic ceramics or composites.

We have studied the cubic phase of  $\text{ZrO}_2/8 \text{ mol } \% \text{Y}_2\text{O}_3$ , one of several samples supplied by T. Negas, by x-ray diffraction to 30 GPa and by optical polarizing microscopy to 300 °C and 15 GPa to investigate its phase behavior and measure its compressibility, both being useful for understanding the HIPing process. Over the pressure and temperature ranges studied, no phase transitions in  $\text{ZrO}_2/8 \text{ mol } \% \text{Y}_2\text{O}_3$  were observed. The pressure dependence of volume for the material is shown in figure 4. The calculated bulk modulus for this material is  $331 \pm 2 \text{ GPa}$ , and its pressure derivative is  $19.8 \pm 0.4$ .

### Ceramic/Glass Emission Standards

In cooperation with D. J. Cronin (Glass Group, Division 561), fluorescent and phosphorescent ceramic/glass standards are under investigation for the U.S. Postal Service. The USPS requires several sets of emission standards to calibrate their primary instruments for detection of emission levels from stamped mail which is sorted and cancelled by their high speed, in-field machinery. This new program has focused on processing of glass/ceramic composites having emission characteristics within the red and green phosphorescent and the red fluorescent range, as well as zero emission materials. Sintered borosilicate glass powders doped with  $\text{Eu}^{3+}$  and with  $\text{Tb}^{3+}$  and sintered  $\text{Y}_2\text{O}_3:\text{Eu}$  plus borosilicate glass constitute candidate materials. Zero-emission candidate materials include Mn, Zn-ferrite spinel and  $\text{Y}_5\text{Al}_3\text{O}_{12}$  (garnet) ceramics.

### Materials for Hot Phosphoric Acid Fuel Cells

This is a new program established by the DOE to investigate materials and corrosion processes associated with first generation, phosphoric

acid fuel cells. Normal construction materials, such as copper, in the cooling segments of fuel cell stacks are subjected to corrosion by phosphoric acid ( $> 150\text{ }^{\circ}\text{C}$ ) electrolyte. In cooperation with D. S. Lashmore and J. Kruger, several candidate protective ceramic oxide and metallic coatings on copper will be fabricated and evaluated for resistance to acid corrosion. Ceramic and metal alloy expertise is provided to DOE for their subcontract engineering design work with Englehardt and United Technologies researchers. Failure analysis of a metal alloy reformer within a 4.5 megawatt fuel cell system at Consolidated Edison, NY, was recently performed.

#### Structural Chemistry Subtask 3 of Task 12156

S. Block, F. A. Mauer, R. G. Munro, and G. J. Piermarini

#### High Pressure Studies of Crystalline, Semicrystalline, and Amorphous Materials

##### Zirconium Oxide

(See Subtask 2, Zirconia-Based Ceramics).

##### Nickel Base Superalloy

In cooperation with Watertown Arsenal, we have measured the compressibility and determined the phase behavior of a nickel base alloy, MAR-M200, by x-ray diffraction to 13.7 GPa. Watertown Arsenal has discovered that MAR-M200, a high strength alloy which has important military applications, loses an appreciable amount of shear strength when shock-loaded beyond 2.8 GPa, its Hugoniot Elastic Limit. MAR-M200 is assumed to be an ideal mixture of two face centered cubic phases,  $\gamma$  and  $\gamma'$ , which have large differences in compressibilities. Thus, when the alloy is subjected to a large stress, as in the case of the firing of a large caliber gun, the differences in the compressibilities of the two phases and/or the possibility of a  $\gamma$ - $\gamma'$  transformation may be the mechanism for the breakdown in the shear strength. Our x-ray results show no indication of a phase transition and no evidence of line-splitting to indicate a compressibility difference effect over the pressure range studied.

##### Indium Bismuth Intermetallic Compounds

In collaboration with J. Jornada of the Institute of Physics, Brazil, an x-ray diffraction study of the high pressure phase transition in the intermetallic compound,  $\text{In}_2\text{Bi}$ , was carried out using the diamond anvil pressure cell and the energy dispersive technique. The 17 kbar reversible transition has been detected previously by resistivity and superconducting critical temperature ( $T_c$ ) measurements. These measurements suggest that the transition involves a decomposition into  $\text{In}_5\text{Bi}_3$  and In-rich phases. However, recent Nuclear Quadrupole Interaction (NQI) measurements by Jornada on the  $\text{In}_2\text{Bi}$  transition can be interpreted as a change to  $\text{In}_5\text{Bi}_3$  structure with 3/48 of the In atoms occupying random positions in the Bi sublattice instead of the proposed decomposition suggested earlier. Our x-ray measurements confirm that the high pressure phase is, indeed, the



$\text{In}_5\text{Bi}_3$  structure. The fact that there was no indication of the presence of any other phase, suggests that the random structure is probably correct.

### Polymers

In collaboration with the Polymer Science and Standards Division, the crystal structures of the high pressure forms of polytetrafluoroethylene (PTFE) and a random copolymer of hexafluoropropylene and tetrafluoroethylene (FEP) were determined. An energy dispersive x-ray diffraction method was employed in conjunction with a diamond anvil high pressure cell. Both high pressure forms were found to consist of planar zig-zag chains, but with unexpected differences in the interchain packing. One possible explanation to account for this difference is a twist in the chain of the FEP copolymer to accommodate the bulk  $\text{CF}_3$  side group. The averaged lateral chain packing in the FEP copolymer becomes hexagonal, thus differing from the orthorhombic packing of the PTFE homopolymer high pressure phase. Compression of the high pressure PTFE phase was measured to four GPa for the first time by an x-ray diffraction method.

### Amorphous and Glassy Materials

There is a class of materials, often called metallic glasses, that is becoming of great interest to industrial and engineering applications. Present indications are that these materials are potentially among the strongest and most corrosion-resistant metals known.

In general, the structure of an amorphous or glassy material can be expressed in terms of radial distribution function. As a result of work initiated in our laboratory at the request of Watervliet Arsenal, this method has been successfully applied to the study of materials at high pressure in a diamond anvil pressure cell. In particular, energy dispersive x-ray diffraction has been used to investigate the structure of amorphous Fe-W (56 wt. % W). The sample was supplied by Watervliet Arsenal. For comparison, the RDF was determined at low pressure (near one atmosphere) in the DAPC and also outside the DAPC at one atmosphere. Figure 5 shows the comparison of the results. Measurements made to 10.5 GPa indicated an approximately linear compression, as shown in figure 6, with an isothermal bulk modulus of 170 GPa (J. Appl. Phys., Sept. 1982).

Presently, in collaboration with D. S. Lashmore of the Electrodeposition Group, this new capability is being applied to amorphous Ni-P which is suspected of having two different amorphous phases, resulting from two different methods of production. This project will attempt to discern a difference between the two samples and then investigate the possibility of a transition between the two under the influence of pressure.

### High Energy Materials RDX

In cooperation with Picatinny Arsenal and the Naval Surface Weapons Center, we are developing methods which permit us to measure and identify decomposition rates and processes in 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX) as a function of temperature and pressure. Nitramine



propellants containing RDX as a binder show complicated ballistic behavior which can effect performance reliability. An anomaly in the burning rate of RDX is observed in the region of 0.3 kbar and is thought to be the result of a change in the mechanism of decomposition. At low pressures, decomposition proceeds predominantly by C-N bond rupture, while at pressures greater than 0.3 kbar, decomposition involves the breaking of N-N type bonds. Depending upon which mechanism is followed, the products of decomposition can be chemically very different. Since large guns operate in the 3 kbar range, to better understand RDX's complex ballistic behavior, it is important to study the effect of pressure and temperature on the thermal decomposition and rate of decomposition of the material.

Our initial approach involved Raman scattering measurements of RDX as a function of temperature and pressure using a diamond anvil pressure cell with a micro-Raman laser technique. The pressure and temperature dependencies of the internal (molecular) and external (lattice) vibrational modes of RDX were measured up to 150 kbar and 175 °C. However, the intensity of the scattering diminished relative to background levels as the melting point was approached, and no scattering from the decomposition products could be measured. Gruneisen parameters for RDX were calculated. Solid residues of decomposed RDX obtained for several different conditions of pressure and temperature were examined by F. E. Brinckman and W. R. Blair (Materials Chemistry Division) using High Precision Liquid Chromatography. Preliminary results indicate that the chemical species in the residues differ and are a function of the decomposition pressure and temperature conditions. The identity of the products is not determined yet. More work in this area is in progress. An infrared absorption method which makes use of a Digital Fourier Transform Spectrometer is being developed and will be used to identify the decomposition processes in RDX.

#### Cadmium Sulfide

The work on the synthesis and high pressure electrical studies of Cl doped CdS sponsored by DOD continued. We investigated several methods of adding Cl to CdS precipitated from  $\text{CdCl}_2$  solution by  $\text{H}_2\text{S}$  or  $\text{Na}_2\text{S}$ . The samples were analyzed by the Center for Analytical Chemistry and sent to Watervliet Arsenal for determination of electrical properties. Calculations of Cd-Cl complexes with a program provided by Dr. F. E. Brinckman and modified by Dr. R. G. Munro, guided the synthetic work.

#### Isothermal Equations of State

It is useful to express the results of high pressure structural studies in terms of isothermal equations of state. Numerous such equations have been proposed in the literature, with each different equation representing different assumptions about the physical system. Usually, it is not easy to determine a priori which of these models is most appropriate for a given material. Least squares fits of these models to a given set of data can yield comparably good fits, while giving significantly different values for the thermodynamic parameters, such as the isothermal bulk modulus. Consequently, it is advisable to consider all of these equations in detail before quoting any one of them as the equation of state.

For that purpose, a FORTRAN code has been developed to analyze lattice parameter and volume data in terms of nine possible isothermal equations of state. A second procedure involving a piecewise regression analysis has also been developed. Applications have already been made to H<sub>2</sub>O-VII and D<sub>2</sub>O-VII (J. Appl. Phys., Sept. 1982), and presently ZrO<sub>2</sub> is being studied. Figure 7 shows an investigation of the bulk modulus of H<sub>2</sub>O-VII and D<sub>2</sub>O-VII using these routines.

### Pressure Measurements at High Temperature

Efforts to develop high temperature capability of the DAPC for application to ceramic materials are currently in progress. One aspect of this work involves improving the accuracy of pressure measurements at high temperature. Measurement of the shift of the ruby R1-R2 fluorescence lines provides the principal means for determining the pressure in a DAPC. The wavelengths and widths of these lines are strongly affected by temperature; and at high temperatures, R1 and R2 overlap significantly. At low temperatures, an additive correction term is adequate to account for the contribution of temperature to the shift of the R-lines, but at high temperatures, the overlap of R1 and R2 introduces larger uncertainties. Consequently, a detailed modeling of the full R1-R2 lineshape, as a function of temperature and hydrostatic pressure, is under study. While several models are suitable, a combined Lorentzian-Gaussian model appears to have several desirable features: speed, accuracy, and adaptability. An example of the compatibility of the model with the observed R1-R2 intensity profile is shown in figure 8. The data points in the figure are connected to form the slightly jagged line, while the model is the smooth dashed line.

### Thermal Diffusion in the DAPC

For experiments performed at high temperatures, it is essential to know how much time would be required to establish thermal equilibrium in a DAPC following a change in temperature. It would also be valuable to know the temperature distribution profiles in the DAPC during the transient heating and cooling periods. These could help identify "hot spots" and "cold spots." For certain work, it would also be useful to know when a temperature variation or gradient would have a real-time duration of a length sufficient for experimental monitoring. To provide estimates for these quantities, a FORTRAN program is being developed specifically for the geometry of the DAPC and its multi-material composition.

### Synchrotron Studies

A new method for obtaining powder diffraction patterns from secondary phases in powders, compacts, and microstructures with improved resolution in the diamond anvil pressure cell is being developed in collaboration with scientists at the Cornell High Energy Synchrotron Source (CHESS).

The method retains the fixed-angle feature of the energy dispersive method which makes it adaptable for use with environmental chambers. Wavelength scanning of the incident radiation for spectral analysis of the diffracted beam is used. Since the energy resolution of a channel cut silicon monochromator is at least an order of magnitude better than



that of a solid state detector system, it should be possible to obtain a substantial improvement in the resolution of diffraction patterns if the divergence of the slit system is kept below about  $10^{-3}$  radians. At the same time, by using a detector with an annular slit to intercept all of the radiation diffracted at a fixed angle of  $2\theta = 12^\circ$ , it is possible to increase the efficiency by a factor of twenty and to reduce the graininess that is typical of patterns from microscopic specimens.

The feasibility of the new method was demonstrated in experiments conducted at CHESS in May of 1981. Count rates as high as 8000 counts per second for the 101 reflection of  $\alpha$ -quartz were obtained, and it was demonstrated that the intensity of the synchrotron radiation was at least  $2 \times 10^4$  times greater than that of the Bremstrahlung from a 12 kW rotating anode source. Patterns were also successfully recorded from samples in the diamond anvil cell. Due to limitations of the monochromator used for the 1981 experiments, we were unable to record any diffraction lines that occurred at energies above 32 keV. Also, because we used an existing detector that severely limited the diameter of the annular slit, we were not able to demonstrate improved resolution.

A greatly improved wavelength scanning microdiffractometer was designed and built at NBS and tested at CHESS in May 1982. Using the A2 line, which has an unusually large monochromator crystal, we were able to extend the range of powder patterns to 50 keV, which, for  $2\theta = 12^\circ$ , corresponds to a d-spacing of 1.18 Å. The resolution was 0.042 keV at 17.7 keV, or 0.24 percent. This is nearly a ten-fold improvement over the resolution obtained in the earlier experiments at CHESS and about four times better than the limit for systems using a solid state detector. Unfortunately, we were unable to obtain a satisfactory pattern from samples in the diamond anvil cell either at high resolution or with the slit widened to approximate the resolution (and count rate) characteristic of the earlier experiment at CHESS. At this time, we are endeavoring to determine why we cannot reproduce our earlier results. Indications are that the difficulty is due to some flaw in the alignment procedure. In particular, we suspect that the expression built into our software to track changes in the height of the beam during the energy scan may not have been adequate. We are particularly anxious to overcome this difficulty because plans are underway for an effective six-fold increase in beam intensity at CHESS. This would greatly enhance the capability of our method of obtaining diffraction data, whereas the energy dispersive method has already reached count rate saturation and cannot benefit.

#### Evaluated Data--Production and Compilation Subtask 4 of Task 12156

C. R. Hubbard, H. M. Ondik, and A. Perloff

#### Standard Reference XRD Patterns

The JCPDS--International Centre for Diffraction Data's Research Association continues to produce highly accurate standard reference powder patterns in collaboration with C. R. Hubbard. NBS Monograph 25, Section 19 will be published in September/October and will contain approximately 50 experimental and one calculated pattern. Over two-thirds of the patterns are designated as "common phases."



During this year, the transition from strip chart recording and measurement to digital data collection and processing has been made. An extensive set of programs has been developed by Dr. N. Pyrros of the JCPDS, in collaboration with Dr. C. R. Hubbard. Program capabilities include second derivative background and peak finding algorithms, interactive and hard copy plotting (fig. 9), internal standard calibration, and interactive PEAKS file editing. These programs are all coupled through the PEAKS file, which contains the results of peak findings. Data files for input to indexing and lattice parameter least-squares refinement programs are also generated. To evaluate and improve the digital methods, over one-half of the patterns of Section 19 were measured and processed both manually and digitally and the results compared. In nearly every case, the accuracy of the digital methods equalled or exceeded the accuracy of the more traditional manual methods. The programs will be the subject of a presentation at the Denver X-ray Conference, August 1982.

The Research Associateship continues to be involved in other activities of the JCPDS. Marlene Morris chairs the Common Phases Task Group which published a revised and updated Common Phases Search Manual in 1982. Use of this search manual speeds phase identification when one or more of the phases of a mixture are in this subfile. All computer based search/match programs also permit searching of this file prior to searching the entire powder diffraction file (PDF). Mrs. Morris is now collaborating with the Forensic Subcommittee to put together a forensic subfile of the PDF. E. Evans and C. R. Hubbard have collaborated with the Least Squares Data Set Task Group to put together a comprehensive set of test data for lattice parameter least-squares. This effort indicates that our least-squares refinement program is operating successfully. Errors in commercial and other programs were uncovered.

#### Critical Reevaluation of the PDF

The PDF is used in thousands of laboratories for phase identification. The file consists of over 38,000 patterns collected over a period of 35 years. C. R. Hubbard, as Data Base Subcommittee Chairman, has been actively involved in the JCPDS five-year project to critically reevaluate the entire PDF and to build a master magnetic data base. NBS activity has been coordinated with the Crystal Data project. Both data centers use the program NBS\*AIDS80 for data evaluation and data bank creation. By June 1982, Dr. W. Wong-ng on the JCPDS and C. R. Hubbard have processed through NBS\*AIDS80 over 10,000 patterns. Another 10,000 will likely be processed by October 1982.

To assist in this project, the JCPDS hired a computer consultant for the summer to add further evaluation routines (e.g., name-formula checking and quality mark assignment) and to process the large number of data at NBS. Data inconsistencies and errors are flagged. When possible, the magnetic data bank will be corrected. If irresolvable errors are found, the phase becomes a candidate for experimental work at NBS or elsewhere.

#### Materials and Components for Fossil Energy Applications

The Fossil Energy Materials and Components Data System consists of two Data Centers operating cooperatively to provide a central source of

materials and components performance and properties data. One element of the system is the Materials Properties Data Center, which is responsible for compiling information on construction materials for coal conversion use and includes data for MHD power generation as time allows. This Center is staffed by personnel from the Materials Chemistry Division (Ondik and Perloff). The major source of data is the Data Center's library of DOE materials research contractor's reports. There are about 50 DOE-funded projects generating materials properties and performance data for coal conversion and utilization. About a dozen of these projects have generated magnetohydrodynamics (MHD) materials data. As time allows, other information sources are sought to expand the data base. Computer storage of the materials properties data base and access to it is handled by a commercial data base management system.

The other segment of the information system is the Materials and Components Plant Performance Data Center, staffed by B. W. Christ of the Fracture and Deformation Division (562). The source of the information consists of reports of materials and component failures submitted to DOE on a voluntary basis by the various coal conversion plants. The information is abstracted and entered into computer storage under a system allowing high speed retrieval with a variety of search schemes. A major use to which the file has been put by requestors of information has been an attempt to correlate operating experience so that trends will be observed indicating primary causes of plant failures for the guidance of designers and operators of coal conversion plants.

The existing computer file of the Materials and Components Plant Performance Data Base contains some 500 reported failures. Although few pilot plants are now operating, resulting in no increase of the data file, there is continuing interest on the part of the user community. Since the data base was started in 1976, hundreds of requests have been answered by distributing over 17,000 computer abstracts and over 800 complete copies of operating event or failure reports. The Center has also given out some 40 copies of reports consisting of sets of abstracts on specific topics, such as corrosion, or for specific materials. Several statistical tables can be prepared by computer from the data base information and over 200 copies of these tables have been distributed.

The major product of the work of the two Data Centers is a book, Construction Materials for Coal Conversion--Performance and Properties Data, an NBS Special Publication SP-642. The book is published as sets of pages, punched with holes to fit standard 3-ring looseleaf notebooks, a format used by a number of other data books. Increasing and revising the data can be done readily on a regular basis. A special binder for the book is available for the looseleaf pages. The publication comprises 600 to 700 pages of data and discussion. This first issue of pages focuses on plant materials data for coal gasification, that form of coal conversion for which there is the largest body of materials data available. The book contains information gained in practical plant experience, as well as the results of materials research and testing programs. It deals with the information in the context of nine separate component areas of the coal gasification plant. The data applicable for a component area is summarized and discussed under that heading. The detailed results of the research and testing programs are included in a separate section



which is divided into four sections covering the major performance and properties data investigated in these programs. These four sections are headed:

- (1) Corrosion Effects, Chemical Reactions, and Phase Changes;
- (2) Erosion, Erosion/Corrosion, and Abrasion Effects;
- (3) Mechanical Properties Testing; and
- (4) Physical Properties Testing.

Each of these sections is divided into subsections for alloys, ceramic refractories, and where such data exist, for coatings. A detailed index to the book lists the materials covered grouped by type. For metals, typical categories are stainless steels, cobalt-based alloys, carbon steel, etc. For refractories, the groupings first list the industrial categories--bricks, castables, etc.--and then the composition. For each material, the various properties are given for which data appear in the book, followed by the reference to the section and page of the book. It is possible to find testing and properties data for specific materials using this index.



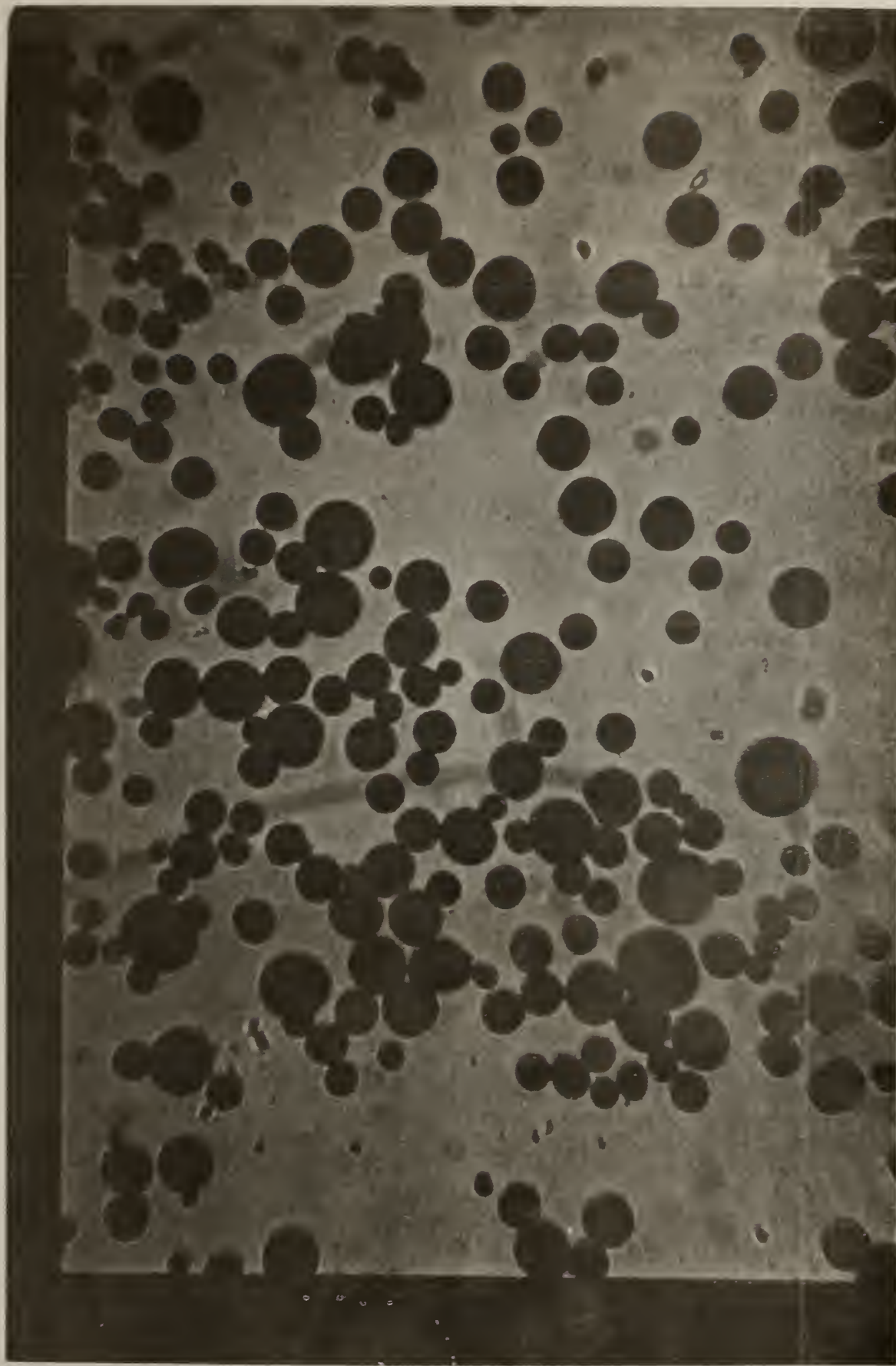


Figure 1 Spray dried, reference, XRD powders as spherical, homogeneous, soft agglomerates ( $< 50 \mu\text{m}$ ).

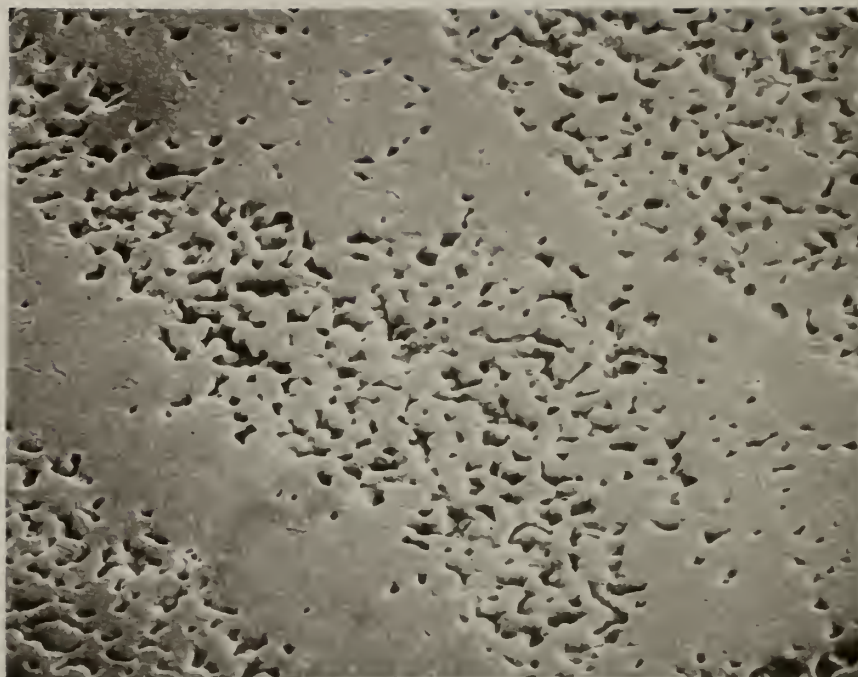


Figure 2 ZrTiO<sub>4</sub> ceramic illustrating differential sintering of partly agglomerated, compacted powder.

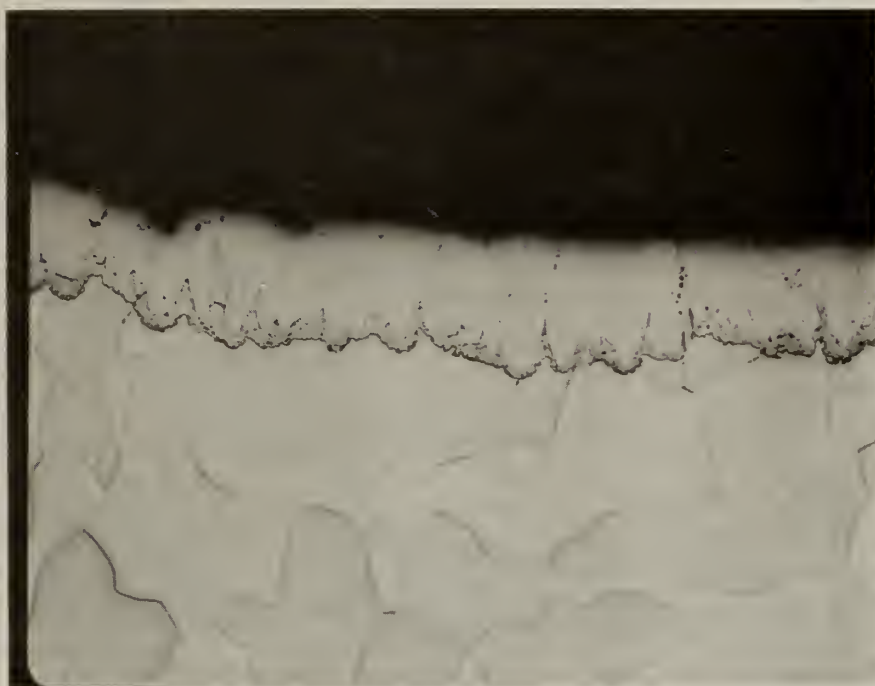
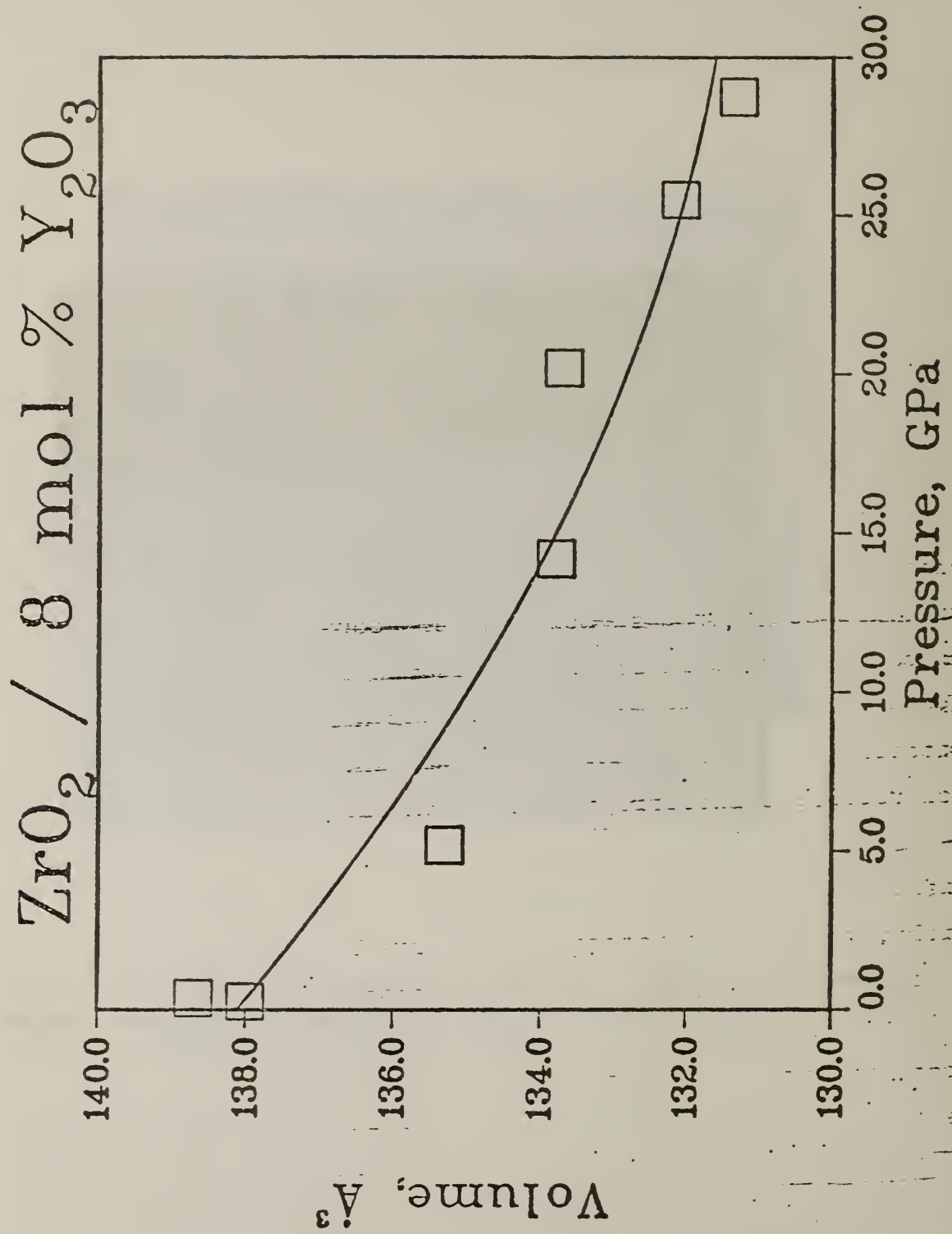


Figure 3 Micrograph illustrating molybdenum silicide, graded coating (upper layer,  $< 0.1$  mm) on the interior surface of a Mo metal tube.





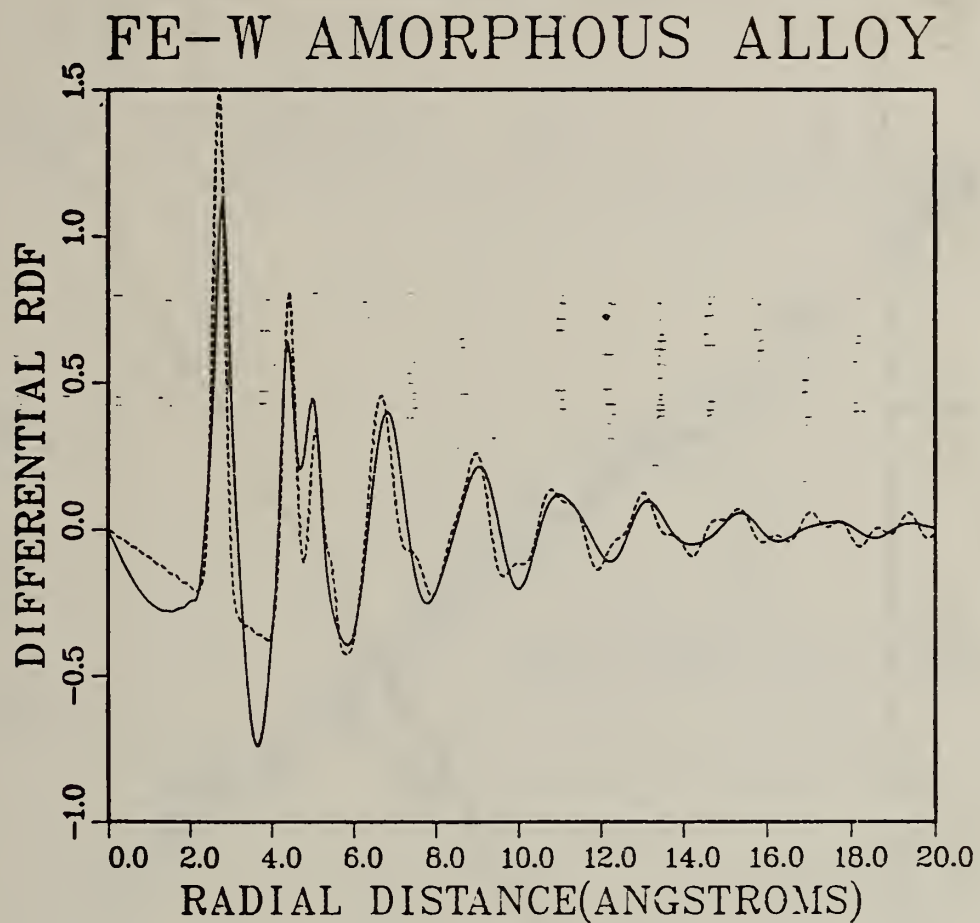


Figure 5 RDF analysis of Fe-W amorphous alloy, comparing results obtained from the diamond anvil pressure cell (DAPC) and from outside the DAPC (dashed line).

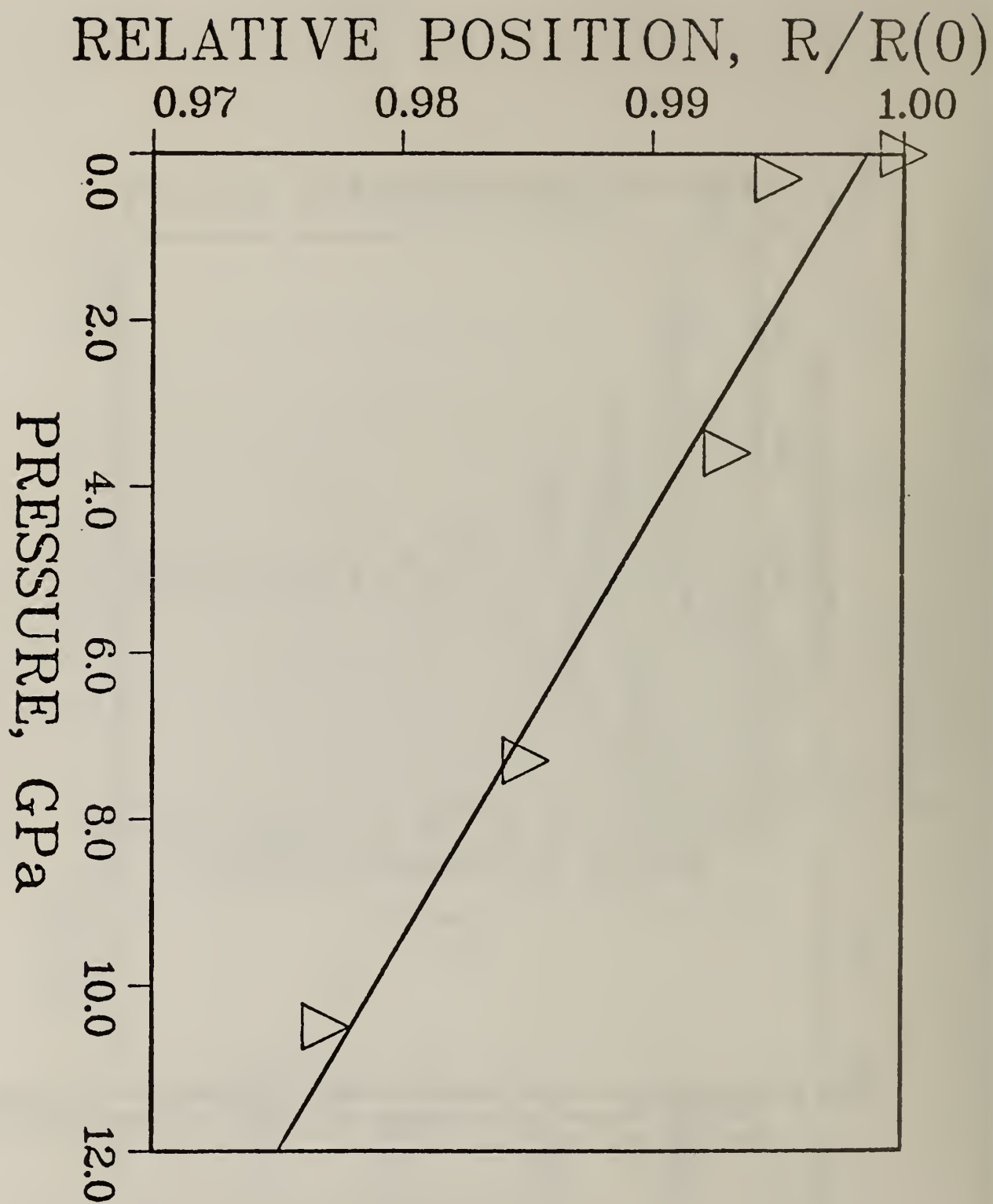


Figure 6 Change in percent peak positions of amorphous Fe-W alloy with pressure.



BULK MODULUS, GPa

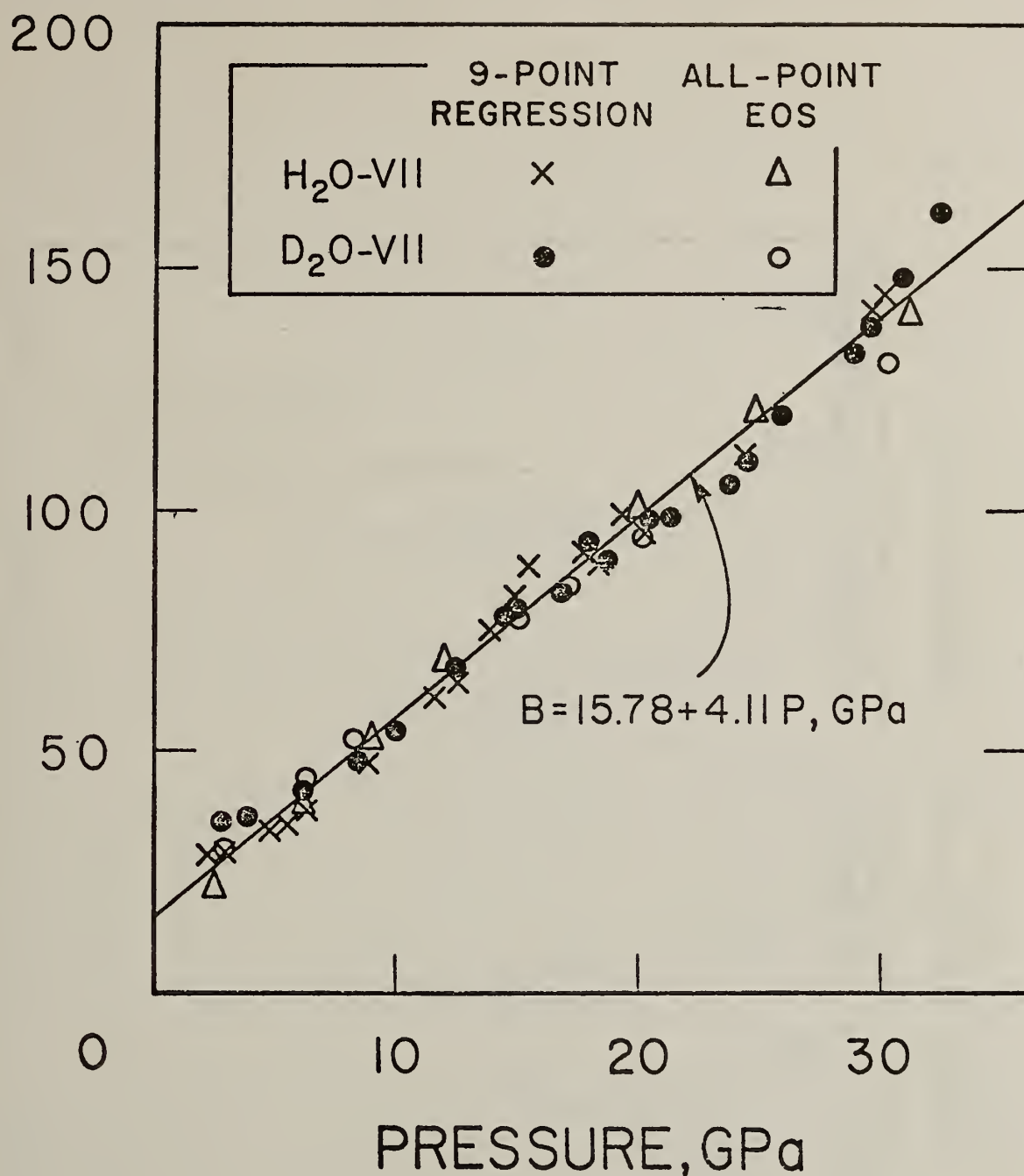


Figure 7 Bulk modulus of H<sub>2</sub>O VII and D<sub>2</sub>O VII as a function of pressure as determined by two methods.

# -----RUBY-R1-R2 LINES MODEL 4

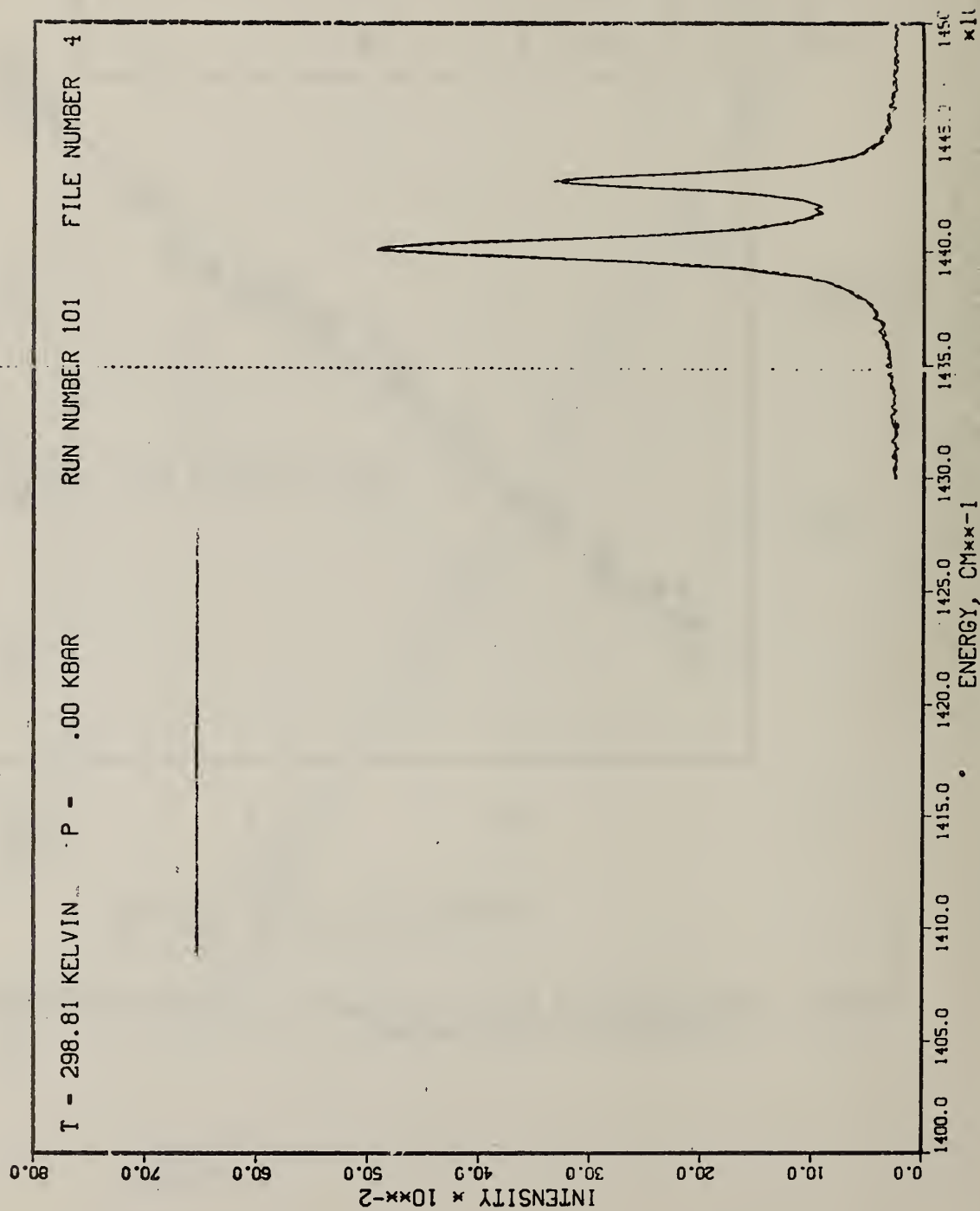


Figure 8 Experimental and calculated ruby R<sub>1</sub>R<sub>2</sub> lines at 298.81 K. Agreement is such that the two overlap

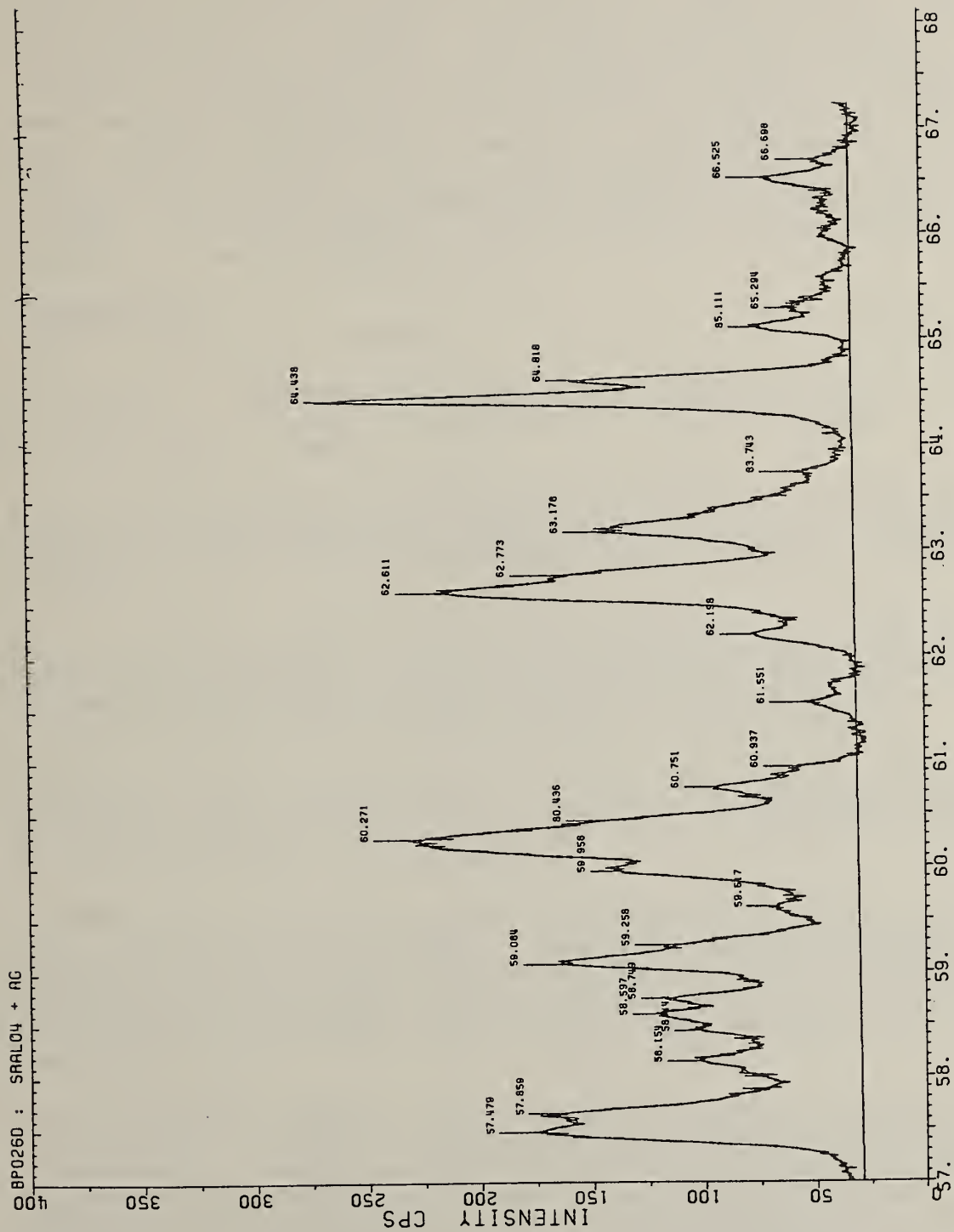
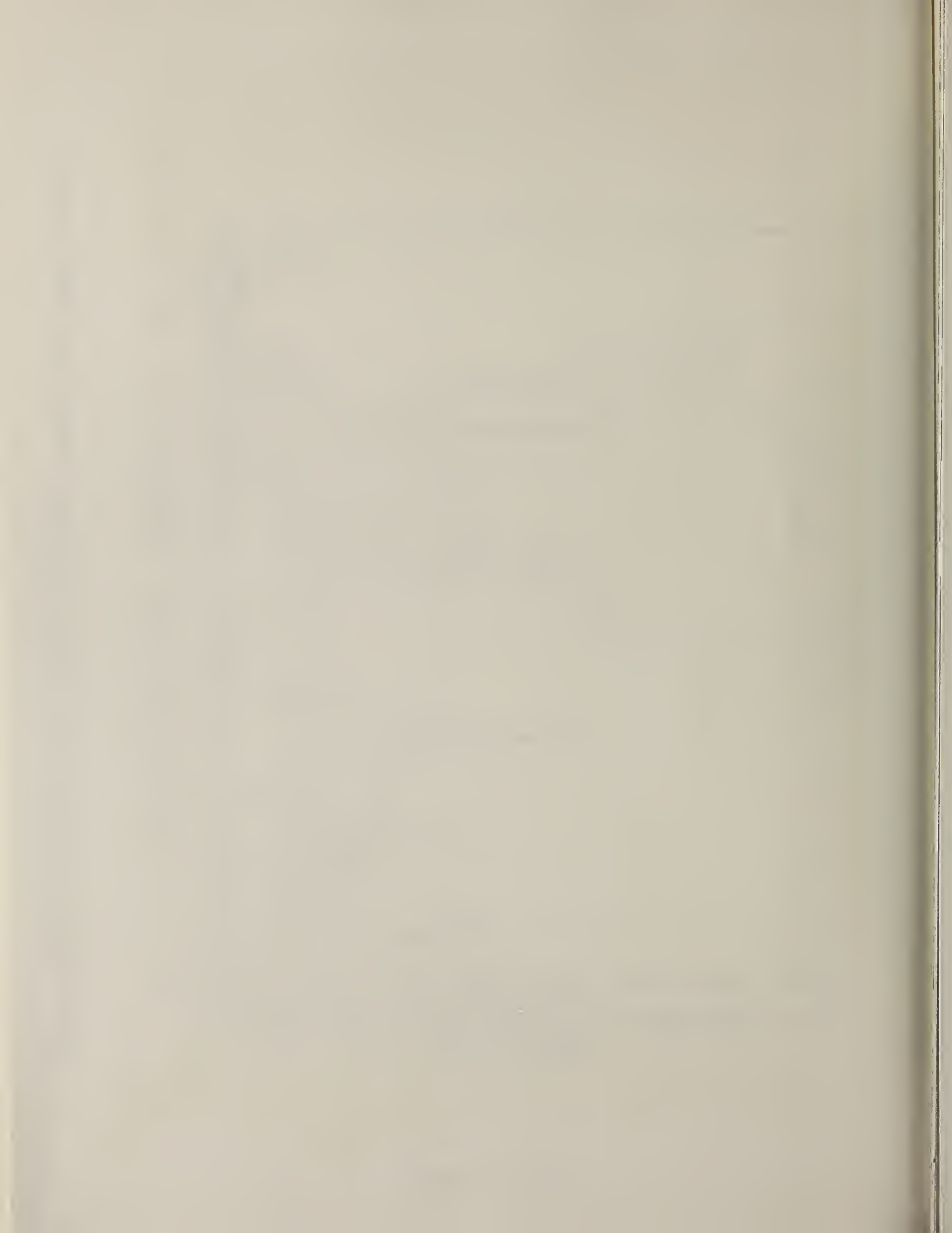


Figure 9 Example of hard copy output including digital data collection and computer processing for standard reference x-ray diffraction patterns.





## RECYCLED OIL PROGRAM--Division 561 Activities

The Tribochemistry Group of the Materials Chemistry Division has the special assignment of providing a technical base of data and measurement methodology to support the Bureau's Recycled Oil Program (ROP). This program is mandated by Congress, under the Energy Policy and Conservation Act, to provide test procedures which can be used to establish the substantial equivalency of virgin and recycled oil products. At the same time, the Group provides, within the Center for Materials Science, major scientific and technical competences in chemical stability of complex organic mixtures at metal surfaces, chemical reaction kinetics in complex condensed-phase systems, friction and wear of materials, tribology, and detailed chemical characterization of complex organic molecules such as lubricants and fuels.

### Tribochemistry

#### Subtask of Recycled Oil Program

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Current technical effort is directed toward development of measurement methods for lubricating oil performance and consistency, and understanding of the mechanisms of lubricant degradation and its effects on friction and wear.

The most important requirement for assuring the quality of re-refined motor oil is development of a set of test procedures capable of monitoring the quality, consistency, and additive response of the lubricating basestocks between periodic engine sequence test qualifications.

At NBS the program is underway in this Group to evaluate the chemical and physical test procedures used on lubricating oil basestocks, as well as to perform research and development on bench-scale performance tests to establish basestock additive response.

In the past year, significant progress has been made in achieving the goals of the recycled oil program. Laboratory evaluation of physical and chemical property test procedures have been completed. The NBS/ASTM basestock consistency study, the most extensive study of its kind, has been completed and the data analysis by statistical methods will be completed this year.

Several laboratory bench tests were developed to simulate full-scale engine dynamometer tests on oxidation stability and wear characteristics of lubricants. A catalyst package consisting of an oxidized, nitrated high boiling fuel fraction and a mixture of metal naphthanates was developed to simulate the chemistry in an operating engine. The concentration and relative proportions of the catalytic components were shown to be critical. Addition of the optimized catalyst package enables several NBS developed oxidation tests to correlate with ASTM engine sequence IIID test results. A plan was developed to produce the catalyst package as a reference material for industry.

Two cooperative studies with industry were conducted in FY82. The NBS/ASTM basestock consistency program was successfully concluded in May 1982. Monthly production samples of lubricating base oils were received from ten refineries (6 re-refined, 4 virgin base oils). Fourteen industrial and Government laboratories participated in analyzing these base oils for consistency and performance. The results of this study are being analyzed by statistical methods. This invaluable database will set a universal criterion for lubricating base oil production quality control world-wide for decades to come. In addition, this database fills a vacuum in addressing batch-to-batch quality control for re-refined base oils, hence fulfilling a key objective in the Congressional mandate of substantial equivalency between re-refined and virgin oil products.

A cooperative study with eleven companies was initiated in April 1982 to study the effects of base oil composition on oxidation stability. Over 100 base oils from ten crude sources were supplied by the companies. Using a NBS developed thin-film oxygen uptake test, statistically significant correlations linking compositional parameters to oxidation stability were established. Interestingly, re-refined base oils from various processes constitute a distinct subset of the base oils. The addition or subtraction of re-refined base oils from the total base oil set did not affect the degree or the nature of the correlations.

In research on the mechanisms of lubricant degradation a gel permeation chromatography-graphite furnace atomic absorption (GPC-GFAA) apparatus was built to study the role of organometallic reactions in wear contacts. Organic iron compounds formed as a result of wear were found to be associated mainly with high molecular weight oxidized hydrocarbon structures (1000 to 100,000 MW). Static oxidation tests also exhibited formation of such organometallic species at high temperatures (200 to 250 °C). A high pressure chemiluminescence apparatus was designed and built to study the kinetics of this interfacial reaction. Fundamental understanding of these reaction mechanisms may hold the key to various technologically significant processes such as corrosion, oxidation, friction, and wear.

Significant advances were also made in the area of separation science of complex organic mixtures. A novel separation method was developed using a neutral activated alumina column and selected solvent systems to separate the naturally occurring polar molecules in fuels and lubricating base oils into their molecular compound classes. Currently a prep HPLC technique is being developed to produce quantities of these molecular specific fractions for performance and stability characterization.

There are three main project areas: Hydrocarbon Separation; Oxidation Stability; and Friction and Wear.

#### Hydrocarbon Separation

Lubricating oil basestocks are complex mixtures of several types of hydrocarbons such as saturates, aromatics, and polars. The composition, especially with regard to the polar type hydrocarbons, is a critical determinant of lubricant performance. The polars are a minor group composed of the most active molecular species in a lubricating base oil.



The structural characteristics of these active species will provide information with regard to its effects on basestock performance.

A novel separation scheme for complex petroleum mixtures such as lubricating base oils has been developed. This new method provides insight and basic information linking molecular structures to oxidation stability and wear. The first step of the separation scheme is to separate the oil into three major fractions: saturates; aromatics; and polars using an NBS developed preparative HPLC procedure. The polar group has been previously determined to have a significant effect on oxidation stability and wear characteristics of the lubricating base oil. A new separation scheme was developed to separate the polar fraction into various molecular compound classes. Three major compound classes were identified: polynuclear aromatic compounds; nitrogen containing basic compounds; and oxygenated polar compounds such as phenols and esters. Each subfraction is studied for performance. The results suggest that the polynuclear aromatic compounds have little effect on oxidation stability but have a higher wear protection. The nitrogen containing compounds have strong anti-oxidant functions, but offer little wear protection. The oxygenated compounds such as esters and phenols have little anti-oxidation property and also offer low wear protection.

The complete separation procedure consists of three steps. The basestock is first eluted on a clay column into saturate/aromatic and polar fractions. The saturate/aromatic fraction is further separated on a dual packed silica gel/alumina column into saturate and aromatic fractions. The last step is the separation of the polar fraction into its subfractions on a neutral alumina column. The mass balance of the separation is good and the fractions produced are ready for performance evaluation.

Spectroscopic methods such as IR, UV, and high resolution mass spectrometry as well as gel permeation chromatography have been applied to elucidate structural characteristics.

### Oxidation Stability

Significantly increased activities in this area in the past year result in several major accomplishments: development of a thin-film oxygen uptake test (TFOUT); development of a differential scanning calorimetry (DSC) oxidation test; development of high pressure DSC instrumentation; degradation mechanism study; the establishment of an NBS/industry cooperative study on base oil composition effects on oxidation stability; and microoxidation and chemiluminescence studies of oxidation.

### A New Oxygen Uptake Method

Lubricating oils currently are qualified through actual engine testing. The Tribochemistry Group developed a thin-film, oxygen absorption test that correlates with the ASTM engine sequence test IIID on oxidation stability, one of the four engine tests that an oil must pass to satisfy automakers' warranty requirements.

The new test provides industry with a valuable research tool for examining various new additive chemistries as well as a valuable screening tool

for new formulations. It is also a key development in meeting the NBS Recycled Oil Program objective. The test provides an economic means to assess the quality consistency of re-refined oils.

The new test incorporates a conventional rotating thin-film oxygen absorption test which simulates the key reaction zone in the high temperature piston ring area. Using a conventional rotary bomb oxidation tester (RBOT) which is commonly available in industry, we modified the hardware to ensure a uniform thin-film oxidation condition to avoid mass transfer effects. Initial results suggested that a catalyst system was needed to simulate the key chemical reactions in an engine. Based on used oil analyses, a combination of lead, iron, copper, manganese, and tin (82, 6, 4, 4, 4 percent respectively) was adopted as a metal catalyst. In addition, research reported by Southwest Research Institute suggested that oxidized fuel components in the blowby gases (combustion gases in the engine combustion chamber leaking through the piston rings) contributed significantly to oil degradation. The final combination of 3 percent metal catalyst and 3 percent oxidized/neutralized fuel components produced results which correlated with the ASTM engine sequence IIID test data. About 20 additional commercial oils were tested and the results indicate that they fell within the expected range of quality.

#### Differential Scanning Calorimetry (DSC) Oxidation Test

A new differential scanning calorimetry test has been developed. Results of the test also correlate with the ASTM Sequence IIID engine test. The DSC test measures antioxidant degradation time in a high pressure oxygen atmosphere (3.6 MPa) in the presence of oxidized nitrated fuel and metal catalysts. The fuel and metal catalysts described above were used to simulate the chemical environment of an operating engine.

The IIID engine test simulates high temperature, high load highway operating conditions and measures oil viscosity increase, deposit formation, and wear. The oil viscosity increase is related to the degree of oxidation of the oil, which is controlled by antioxidant additives in the oil. Viscosity increase is very slow until antioxidants are depleted, whereupon the viscosity increases very rapidly. Thus, the time to a critical viscosity increase (375 percent in the IIID test) can be related to the antioxidant lifetime.

The DSC test provides an oxidation induction time which reflects antioxidant depletion time. The observed induction time and the precision with which it can be determined are dependent on the temperature and pressure at which the test is performed. The observed induction time decreases with increasing temperature and oxygen pressure, but precision improves. The optimum conditions for correlation with IIID engine tests were 175 °C and 3.62 MPa oxygen.

DSC measures the rate of heat evolution or consumption by thermal events occurring in a sample. Oxidative degradation of an oil proceeds by a complex free-radical chain-reaction mechanism which includes some very energetic exothermic steps. Antioxidants provide rapid, low-energy alternative reaction paths which produce relatively little heat. After the antioxidant is depleted, autocatalytic chain-reactions proceed and



the rate of exothermic oxidation rapidly increases with time. In a DSC test, the DSC signal is essentially constant until antioxidant is consumed, then rises sharply as autocatalytic degradation accelerates. The antioxidant depletion point is marked by the sharp rise in the DSC signal.

Correlation of DSC results with engine tests was demonstrated by DSC tests of ASTM IIID reference oils of known engine performance. DSC induction times correspond to the IIID time to 375 percent viscosity increase.

#### High Pressure Power-Compensation DSC Instrumentation

A high pressure modification of a commercial power-compensation DSC has been developed. In order to effectively study thermal oxidation of lubricants and fuels by DSC, pressures up to 4.5 MPa were needed. High pressure heat-flux DSC has been commercially available for several years; but high pressure power-compensation DSC has not. Attempts by manufacturers and users of power-compensation DSC to operate at pressures greater than 2 MPa have produced severe instability in the DSC signal. The new instrumentation can operate up to 5 MPa.

Differential scanning calorimetry detects thermal events (reactions, phase transitions, etc.) which occur in a sample by comparing the sample to a stable reference. Power-compensation DSC measures the difference in power required to maintain the sample at the same temperature as the reference. The power-compensation DSC has sample and reference pans in separate cavities in a heat sink. Purge gas enters below the pan, flows upward past the pan, and out through holes in the cover of the heat sink. Signal instability can be caused by time-dependent dissimilarities in the thermal environments of sample and reference pans. Near ambient pressure, no instabilities occur. At higher pressures, however, the flow and thermal properties of the purge gas are much different than at lower pressures. Flow and convective turbulence near the sample and reference pans cause significant time-dependent fluctuations in the thermal environments.

Turbulence was minimized in the NBS instrument by altering the flow path of the purge gas. Signal instability was reduced by a factor of 350 to levels typical of ambient pressure operation. No reduction in detector sensitivity resulted, however. Temperature calibration is affected by high pressure, but in a repeatable fashion which can be corrected by calculation or adjustment of instrument controls.

The development of the high pressure modification has been greeted with enthusiasm by the manufacturer of the DSC and by users interested in pressure DSC applications. We have applied the pressure DSC to the development of new test methods for the evaluation of synfuels and automotive lubricants.

#### Lubricant Degradation Mechanism

Highly formulated lubricants are often used to lubricate various high load, high stress modern engines in various power trains. One of the



major causes of premature engine failure is lubricant breakdown which causes corrosion, fatigue, wear, and sometime sudden seizure/ welding. The object of this project is to develop test methods to measure and understand the degradation of lubricants and their relationship with engine wear/failures.

Conventional oil analysis techniques include infrared spectroscopy and wear metal analysis by emission spectroscopy or ferrography. Emission spectroscopy measures metal particles mostly less than 1  $\mu\text{m}$ . Ferrographic methods are effective only for iron (magnetic) wear particles at 1  $\mu\text{m}$  or above. All three techniques function reasonably well in clean oil systems. With normal used oils contaminated by airborne particles, oxidized oil components, and wear particles, analysis becomes difficult. Recent ASTM round-robin results on oxidation and nitration in used oils by infrared spectroscopy indicated complete disagreement among a score of oil company laboratories. One major technical problem is how to set condemning limits for various parameters that are measured. High levels of wear metals in used oil indicate incipient seizure and the time to failure may be very short. Oil analysis usually measures oxidative degradation and sometimes contamination, but their relationship to wear and failure are not clear.

During the past year, some key experiments were performed. A carefully selected lubricant with known engine performance was degraded in the laboratory under controlled conditions. Various state-of-the-art measurement techniques as well as conventional oil analysis methods were used to follow the degradation pathway of the oil. Periodic samples were withdrawn and tested in NBS developed laboratory engine simulation tests. We found a definite correlation between additive depletion and increase in wear. Secondary interactions between additive decomposition products and base oil oxidation products were able to provide additional wear protection but not to maintain the load carrying capability of the lubricant. Results are shown in figures 1 and 2.

In figure 1, (from left to right) the viscosity of the oil remains relatively stable until about 120 hours. At that time, the viscosity increases sharply to over 800 percent of the original oil viscosity. The antioxidant capacity is measured by the Ford free-radical titration method [1] which measures the ability of the oil to eliminate free radicals. We see that the antioxidant capacity drops sharply under oxidation at about 50 hours (antioxidant depletion/degradation). However, it rises again to about half of the original values. This suggests secondary reactions between the base oil and additive degradation products to regenerate antioxidant species. The seizure load [2] indicates the capacity of the lubricant to carry a certain load without seizure. The data in figure 1 suggest that the seizure load decreases by 30 percent in the first 50 hours coincident with the additive depletion. After 50 hours, test results suggest frequent seizures and erratic friction traces and a clear seizure load was difficult to determine. The amount of wear increases about 30 percent and remains level after 50 hours. Differential infrared results on the phosphorus-sulfur bond (characteristic of the anti-wear additive zinc dithiophosphate) suggests that the anti-wear additive is exhausted in the first 50 hours. This confirms the observed wear and seizure load measurement.

In figure 2, additional parameters measured in the same experiment are presented. The viscosity increase and the antioxidant capacity are shown for reference. The oxidation induction times are measured with the NBS developed thin film oxygen uptake test which has demonstrated correlation with engine oxidation results [3]. The oxidation induction time drops quickly and reaches a minimum at about 20 hours. This decrease in oxidation stability suggests additive depletion and is in agreement with the antioxidant titration results. After 20 hours, the oxidation stability of the oil increases gradually, again suggesting antioxidant regeneration. Differential infrared measurements on carbonyl (carbon-oxygen bond) suggest a continuous rise in the oxidation process independent of other processes. The total acid number measures the organic acidic species formed under oxidation. The data in figure 2 indicate stepwise increases with different slopes. The acidic species begin to form at about the 75th hour with a steep slope. At about the 120th hour, the formation rate decreases and the viscosity increase begins to rise sharply. Average molecular weights as measured by GPC indicate a constant level until about the 130th hour.

These results are interesting and significant. Contrary to conventional theories, drastic failure did not occur when all the additives were exhausted. In fact, the original additives were exhausted in the first 40 hours, yet the viscosity failure did not occur until about 120 hours. Coincident with the viscosity increase, the acidic species in the oil reach a certain level (TAN = 12). The load carrying capacity, however, appears to correlate with the additive depletion.

Controlled experiments with a single lubricant degradation suggest some condemning limits on used oil properties. Three new test procedures have been developed and proven useful in oil analysis for engine condition monitoring. Future work will test other lubricants and additives in an oxidation/wear coupled system.

#### NBS-Industry Cooperative Program on Lubricating Base Oil Composition Effects on Performance

Results of this NBS work were reported at the ASTM Committee D-2 on Fuels and Lubricants meeting held in Phoenix, AZ, in December 1981, and extensive interest was expressed by oil companies and the additive industry. A cooperative study has been initiated between 11 companies and NBS to relate chemical composition of lubricating base oils to performance. This effort will capitalize on the NBS thin-film oxidation test to study the effects of base oil chemical compositions on oxidation stability.

The relationship between chemical composition of base oils and performance is not now understood. On the average, only about two percent of the selected crudes can be processed into lubricating base oils. Current practice calls for constant crude source and processing technology to ensure quality. Each crude source change necessitates a complete engine testing of all products for requalification. Sometimes the products have to be modified and redeveloped. A basic understanding between composition and performance can suggest alternate processing technology to remove undesirable compounds and improve product performance.



Various re-refined lubricating base oils derived from different process technology were used in conjunction with a commercial additive package. Analytical data on chemical composition were gathered and correlated with performance on oxidation stability. Single components as well as combinations were tested. Initial results indicated that polar compounds, sulfur compounds, and aromatic compounds were critical to performance. Straight line correlation with a correlation factor of 0.95 was obtained for the predicted and measured oxidation stability using these re-refined base oils. Additional data on a few virgin base oils, however, were insufficient to establish a separate correlation for virgin base oil performance from different crude sources.

In the cooperative program, nine companies sent over 100 base oils to NBS with associated analytical data. These virgin oils from various crude sources and processing technologies were tested in the TFOUT and the results correlated with the composition parameters. New insights were gained from the various functional dependencies of the parameters. The amounts of saturates and sulfur compounds were shown to have the major influence on the base oil response to additives.

#### Microoxidation Test and Chemiluminescence Studies

Oxidation of lubricating base oils has been a primary research area during the past year. A study of the effects of iron and copper on oil oxidation was carried out using the Penn State microoxidation test. This is a high temperature, thin-film test that simulates the conditions in the cylinder wall/piston ring area of an engine. Tests on steel, copper, and glass substrates showed iron to be a pro-oxidant and copper to be an oxidation inhibitor under the conditions of the test. The study also shed new light on the overall mechanism showing that the process is comprised of three parts: primary oxidation; polymerization of the oxidized products; and formation of oil insoluble products. Previously polymerization and formation of insolubles have been considered to be part of the same process. This work showed that while large amounts of high molecular weight products were formed on glass, the subsequent formation of insolubles required the presence of metals. Interestingly, copper which inhibited primary oxidation was found to be the stronger promoter of insolubles formation.

Further oxidation research is being undertaken using chemiluminescence (CL), light given off by the reaction. The application of CL on liquid phase oxidation of complex molecules is new and shows much promise as a simple, sensitive, non-intrusive method for continuously monitoring the oxidation process. Work this year has included preparation of an extensive literature review of CL, and design and construction of two instruments, a general-purpose CL oxidation apparatus and a high-pressure oxidation cell in which CL is measured remotely via a fiberoptic probe. This fiberoptic CL technique has exciting research implications as such probes could potentially be placed into harsh environments such as automobile engines to study oil degradation under actual service conditions.

The general-purpose CL apparatus is modular in design with interchangeable reaction cells. It is currently set up to study the hydrocarbon-metal interface reactions and the basic mechanisms in organometallic species



formation. Techniques have been developed for calculation of activation energies for both the initiation and propagation steps of the oxidation chain reaction. In addition, the integral of the CL curve is apparently proportional to the overall conversion measured by other thin film oxidation tests.

### Friction and Wear

Emphasis here has been in two areas: development of laboratory bench test methods to study the friction and wear characteristics of model compounds and lubricating oils; and elucidation of the chemical interaction mechanisms between lubricants and metal surfaces in wear contacts.

Two new microsample thin film wear tests were developed to study the oxidation-wear coupled performance of lubricating oils. These tests use only six microliters of sample for each test. A microsample step loading seizure test measures the load carrying capability of the lubricant. The other test, measured the time to seizure for lubricants under boundary lubrication conditions. Results of both tests correlate with ASTM engine sequence IIID test wear results.

A microsample sequential test is currently being developed to measure the coefficient of friction modified lubricants, additives, model compounds, and chemically active components derived from basestocks. Preliminary tests are underway to measure the coefficient of friction of a set of formulated lubricants with friction modifiers, demonstrated in engine tests to have fuel economy benefits.

A study was conducted to determine the additive response of different basestocks in friction and wear. The step loading seizure test which had demonstrated correlation with engine test was used. It was found that at low additive package concentration (0.5 percent), the different basestocks gave different friction and wear values for the same additive.

A new wear debris analyses technique was developed to analyze the wear products in a contact junction for organometallic components. This technique combines gel permeation chromatography with graphite furnace atomic absorption chromatography to determine the molecular weight range of iron containing organometallic species under both static and dynamic rubbing conditions.

### Static Oxidation Test

Metal and metallo-organic compounds are known to play important roles in oxidation stability and degradation processes in lubrication. However, detection systems previously employed were non-specific for metal-containing species that are generated during interactions between metals and lubricants. A high sensitivity analytical system designed for such purpose was built. Key features of the system involve separation of analytes by high-performance size exclusion chromatography and continuous effluent analysis of central metals or metalloids by graphite furnace atomic absorption spectrophotometry. Auxiliary nonspecific and nondestructive detectors, i.e., refractive index and ultraviolet were also incorporated.

This approach was successfully applied to the static, thin film oxidation reaction products. During this test 40 microliters of oil were added to a metal disc 1.9 cm in diameter, contained in a glass reactor at 225 °C under an air flow of 20 cc/min. The oil formed a 150 µm thin film on the metal disc. After selected time intervals, reaction was quenched, a solvent was added and the resulting solution was filtered and analyzed with a SEC-RI-GFAA system. Figure 3 illustrates typical data generated from this system when applied to oxidation on a copper disc for 15 minutes at 225 °C. Information may also be gathered on the distribution and concentration of metals in the high molecular weight products as a function of time. This is illustrated for copper in figure 4. Studies involving steel discs have provided data on metal uptake and molecular weight distributions of high molecular weight products as shown in figure 5. In all cases, the metal was shown to exist mainly in the high (1000 to 100,000 MW) region. There was also different behavior for copper and iron. In figure 4, the concentration of copper organometallic compounds appear to decrease with time while the iron organic compounds appear to increase with time (fig. 5).

#### Dynamic Rubbing Wear Test

The same analysis procedure was applied to a microsample thin film wear test conducted at room temperature for a fully formulated motor oil. The wear test was stopped at different times and the wear debris was analyzed. The results are shown in figure 6. The iron again appears in the same molecular weight region as in the static case with similar patterns. This suggests high molecular weight metal-organometallic compounds are formed in wear contacts at room temperature and the mechanisms appear to be similar to the static case at high temperatures. This further implies that the temperature at the wear contact is considerably higher than the room temperature confirming the existence of high "flash temperatures" in the contact zone.

- [1] Mahoney, L. R.; et al. The determination of the antioxidant capacity of new and used lubricants: method and application. Ind. Eng. Chem. Prod. Res. Dev. 17: 250; 1978.
- [2] Gates, R. S.; Hsu, S. M. Development of a four-ball wear test procedure to evaluate automotive lubricating oils. ASLE Preprint No. 82-AM-6A-4, presented at the ASLE meeting; Cincinnati, OH. 1982 May.
- [3] Ku, C. S.; Hsu, S. M. A thin-film oxygen uptake test for the evaluation of automotive lubricants. To be presented at the ASLE/ASME joint conference; Washington, DC. 1982 October 7-9.

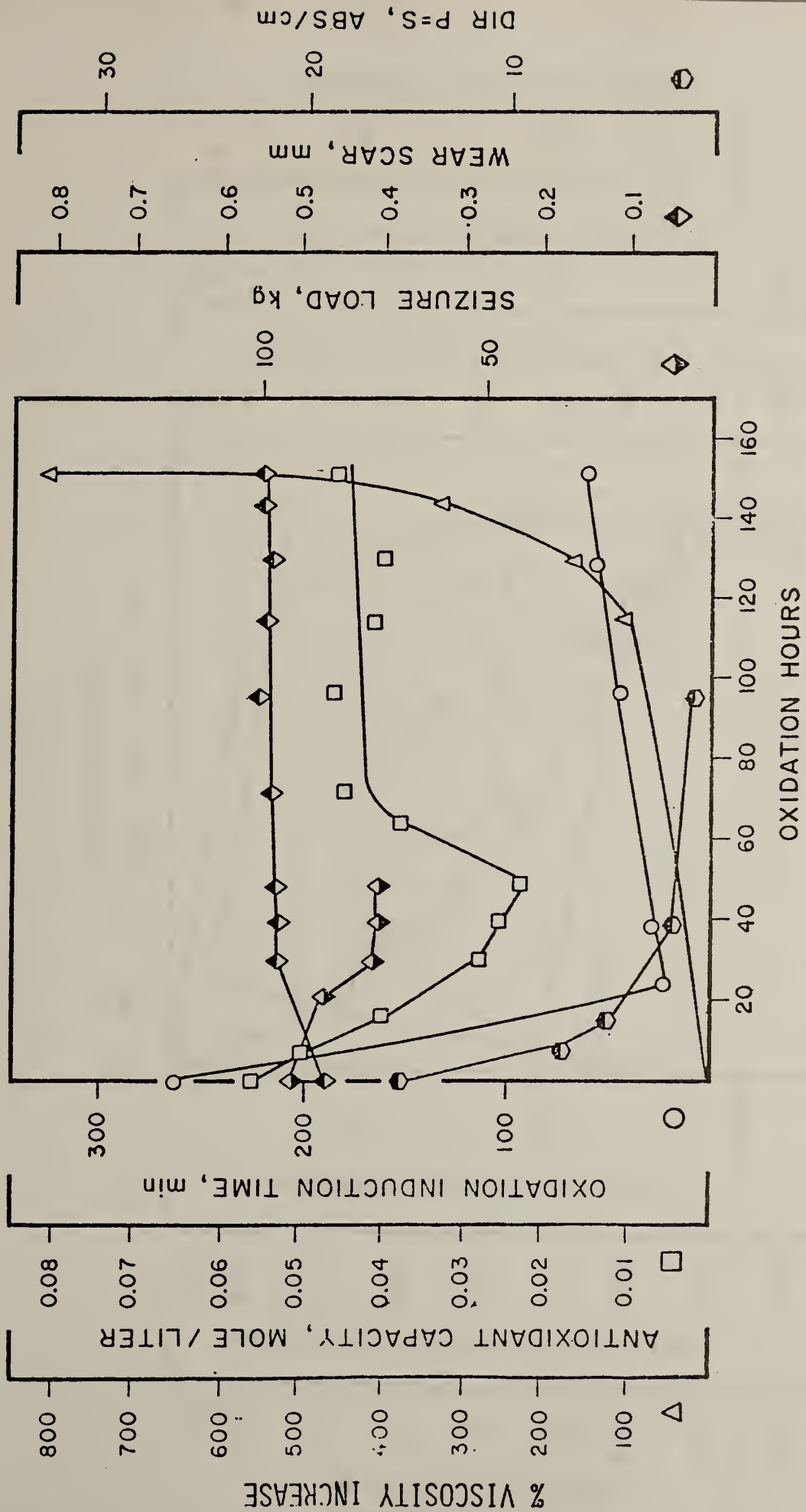


Figure 1 The effects of degradation on wear.



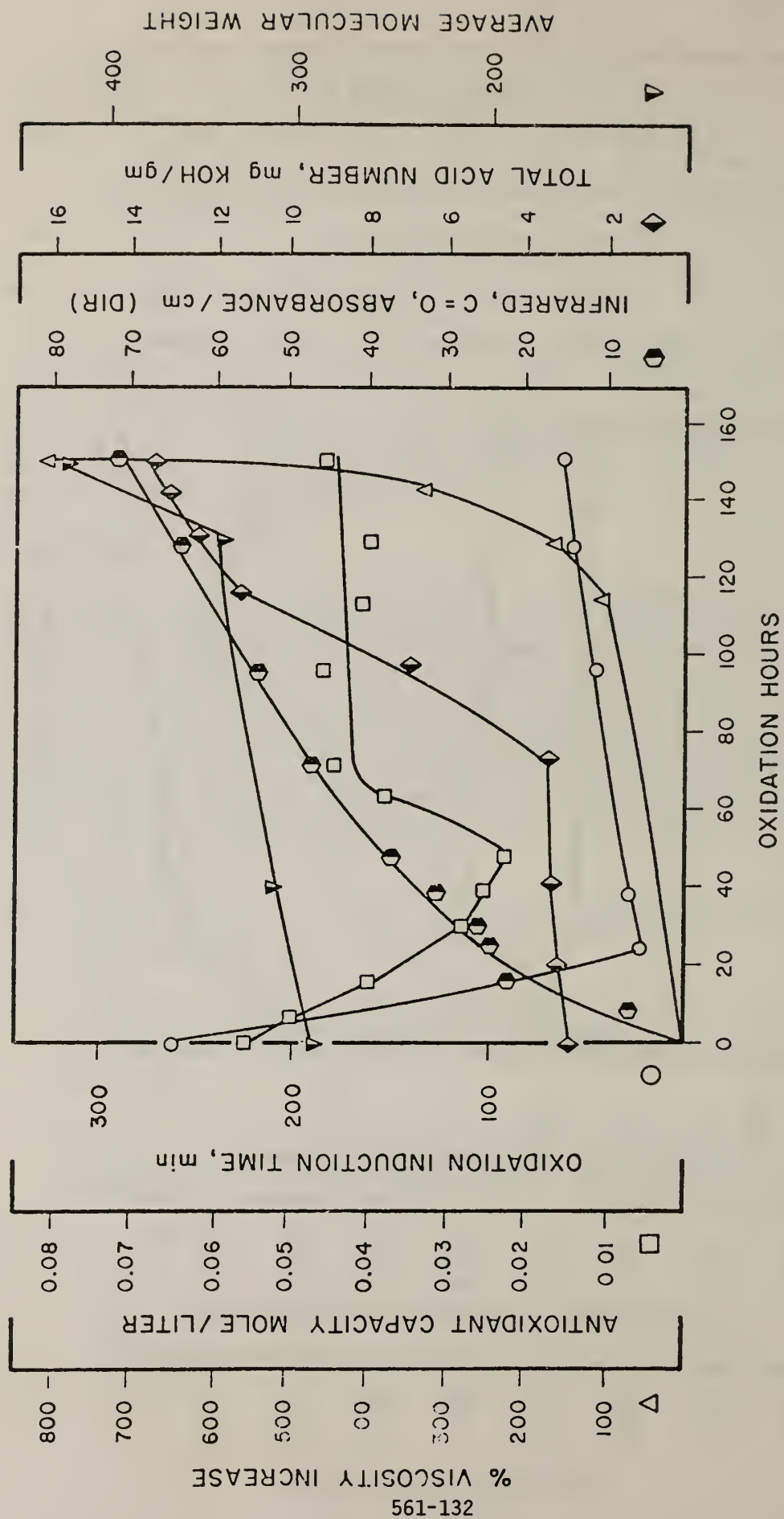


Figure 2 The effects of degradation on oil properties.

— VIRGIN BASE OIL  
---- OXIDIZED OIL (15 min)

RI

0

Copper

0

AA

233 K

37 K

3 K

395

220

254

MW DISTRIBUTION

Figure 3 Static thin film oxidation copper-hydrocarbon interactions.

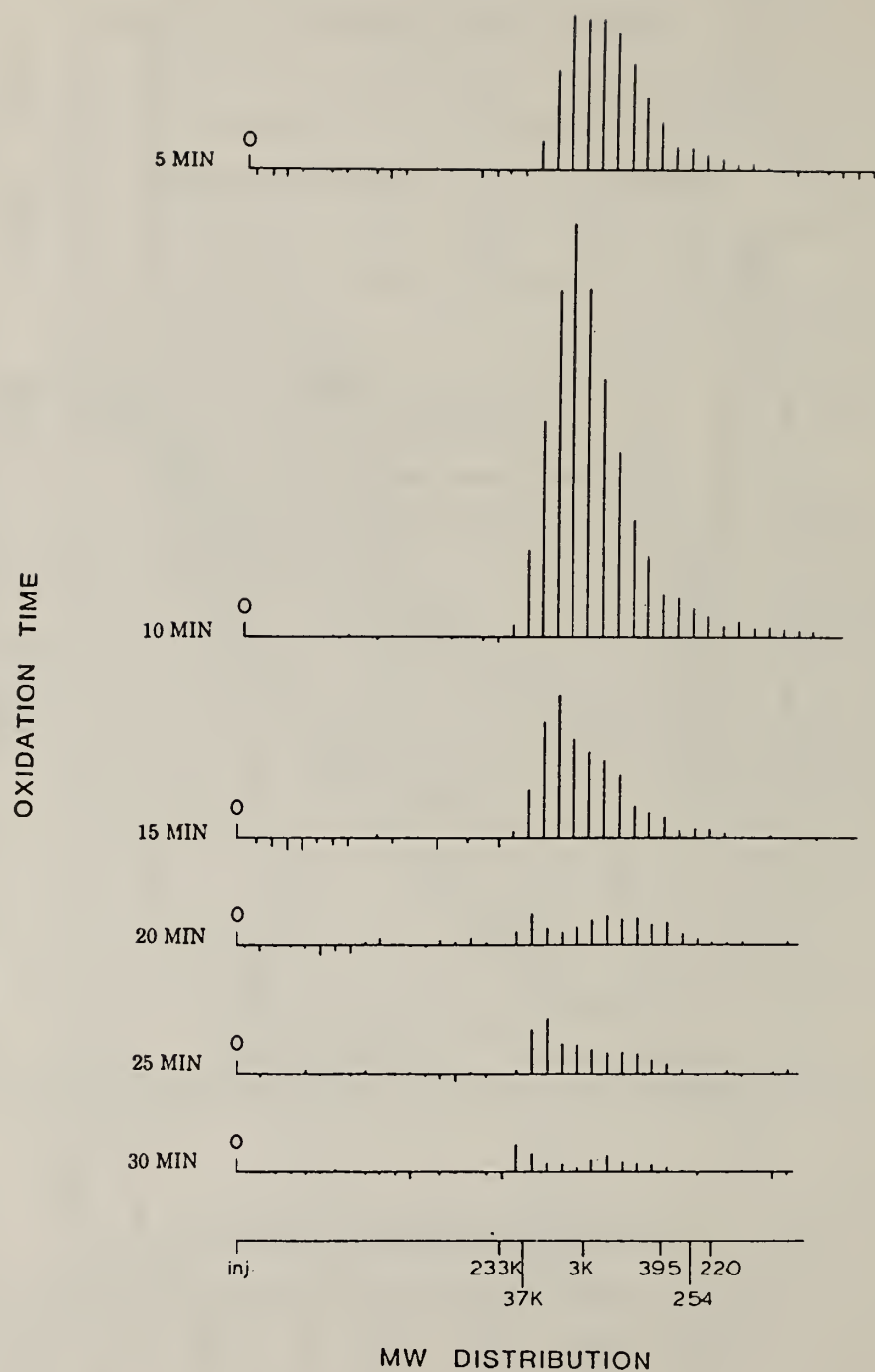


Figure 4 Static thin film oxidation copper concentration and distribution as a function of oxidation time.



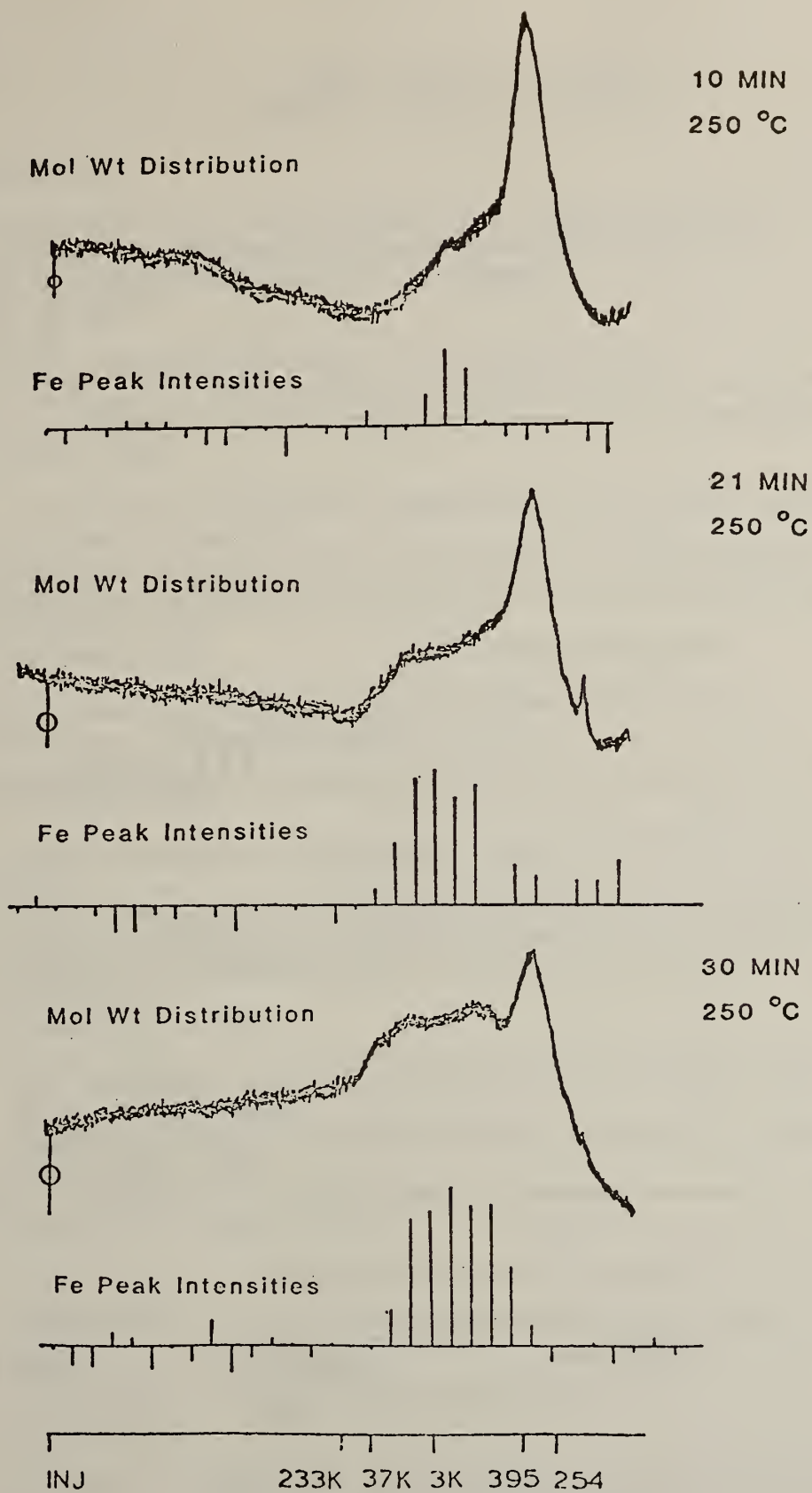


Figure 5 Static thin film oxidation iron-hydrocarbon interactions.

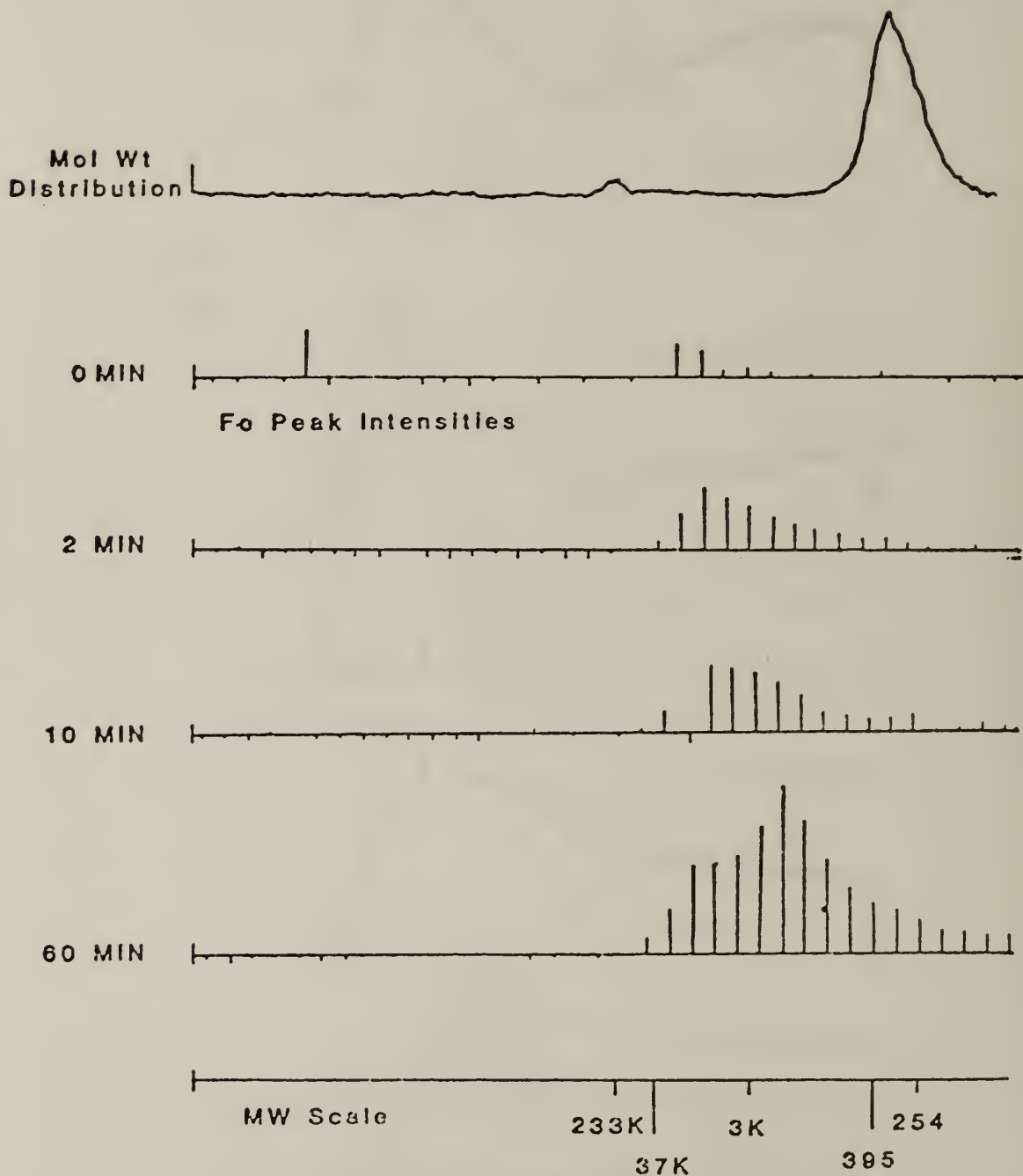


Figure 6 Dynamic thin film wear test iron-hydrocarbon interaction: REO 76A-1.

Other Activities of the  
Materials Chemistry Division

Invited Talks

A Rational Function Approximation of Powder Diffraction Profiles  
American Crystallographic Association, Washington, DC  
N. C. Panagiotopoulos and C. R. Hubbard  
March 1981

JCPDS-International Centre for Diffraction Data  
International Union of Crystallography, Ottawa, Canada  
C. R. Hubbard  
August 1981

An Assessment of Materials Requirements and Research Needs for Open  
Cycle MHD Systems  
Symposium on the Chemistry of Materials at High Temperatures, Harwell,  
Cambridge, England  
S. J. Schneider  
September 1981

Ellipsometric Studies on the Air-formed Film on Iron  
Bell Labs., Murray Hill, NJ  
J. J. Ritter  
September 1981

On the Mechanism of Transgranular Stress-Corrosion Cracking in Alpha-  
Brass  
Second International Conference on Environmental Degradation of  
Engineering Materials, Virginia Polytechnic Institute and State  
University, Blacksburg, VA  
E. N. Pugh  
September 22, 1981

Time Evolution of the Atom Density "Hole" Following Laser Enhanced  
Ionization in Flames  
Federation of Analytical Chemistry and Spectroscopy Societies (FACSS),  
Philadelphia, PA  
J. C. Travis, G. C. Turk, and P. K. Schenck  
September 24, 1981

X-ray Analysis of Selected RDF and Coal Samples as a Function of  
Temperature  
Symposium on Resource Recovery and Environmental Issues of Industrial  
Solid Wastes, Oak Ridge, TN  
C. R. Robbins, E. Domalski, and R. Kelly  
October 1981

Information Systems for Fossil Energy Materials Applications  
Sixth Annual Conference on Materials for Coal Conversion and Utiliza-  
tion, National Bureau of Standards, Washington, DC  
H. M. Ondik  
October 1981



Arc Plasma Sprayed Ceramic Coatings  
Sixth Annual Conference on Materials for Coal Conversion and Utilization, National Bureau of Standards, Washington, DC  
T. Negas  
October 1981

Unusual Luminescence Behavior of Terbium Phosphate Glasses  
Fall Meeting, American Ceramic Society, Bedford Springs, PA  
D. J. Cronin, D. H. Blackburn, and W. K. Haller  
October 2, 1981

Graphics on the 9825 Computer  
Desktop Computer Users Group, Hewlett Packard Co., Rockville, MD  
P. K. Schenck  
October 6, 1981

Optogalvanic Spectroscopy  
Highlands in Chemistry Seminar, Virginia Polytechnic Institute, Blacksburg, VA  
P. K. Schenck  
October 8, 1981

Powder Processing of Potassium Aluminosilicate  
Fall Meeting, Basic Science Division, American Ceramic Society, Louisville, KY  
L. P. Cook  
October 11, 1981

SEM, TEM, and STEM Investigation of Sintering in Anorthite  
Fall Meeting, Basic Science Division, American Ceramic Society, Louisville, KY  
L. P. Cook  
October 12, 1981

Research Applications of High Pressure Sampling Mass Spectroscopy to Cluster Nucleation  
NBS Aerosol/Small Particle Seminar, NBS, Washington, DC  
D. W. Bonnell  
November 1981

Mass Spectrometric Studies of MHD Slag Thermochemistry  
MHD Specialists Meeting, Sydney, Australia  
J. W. Hastie  
November 1981

Why A Career In Chemistry?  
Department of Chemistry, Western Maryland College, Westminster, MD  
J. A. Jackson  
November 4, 1981

Speciation of Arsenic in Fossil Fuels and Their Conversion Process Fluids  
Arsenic Symposium, sponsored by Chemical Manufacturing Association and NBS, National Bureau of Standards, Gaithersburg, MD  
C. S. Weiss  
November 6, 1981

Mechanisms of Stress-Corrosion Cracking in FCC Alloys  
Materials Frontier Seminar, North Carolina State University, Raleigh, NC  
E. N. Pugh  
November 13, 1981

Preparation of Thin Amorphous Films by E-Beam Evaporation from  
Multiple Sources  
13th Boulder Laser Damage Symposium, Boulder, CO  
E. N. Farabaugh, D. M. Sanders, M. E. Wilke, S. A. Hurwitz, and  
W. K. Haller  
November 17, 1981

Index, Thickness, and Birefringence of Thin Films by Guided Waves  
13th Boulder Damage Symposium, Boulder, CO  
A. Feldman and E. N. Farabaugh  
November 17, 1981

Test Methods for Lubricant Degradation  
American Society of Lubrication Engineers, Baltimore Section Meeting,  
Baltimore, MD  
S. M. Hsu  
November 19, 1981

Physics and Chemistry of a Thin Film Wear  
Wear Topical Conference Meeting, Poster Session, American Physical  
Society, New Orleans, LA  
R. G. Gates  
November 23-24, 1981

Recent Advances in High Temperature Chemistry  
Chemistry Department, University of Tasmania, Sydney, Australia  
J. W. Hastie  
December 1981

Use of MHD Materials Science Development in Other Technical Areas  
AIAA, Colorado Springs, CO  
S. J. Schneider  
December 3, 1981

Relationship Between Composition and Performance for Re-refined Base  
Oils  
American Society for Testing and Materials Annual Meeting, Committee  
D-2, Phoenix, AZ  
S. M. Hsu  
December 10, 1981

Electrochemical Noise Measurements  
Conference on Electrochemical Methods in Corrosion Testing and  
Research, Manchester, United Kingdom  
U. Bertocci  
January 5, 1982

The Molecular Speciation of Trace Elements in Synthetic Fuels  
Mobil Corporate Research Center, Princeton, NJ  
C. S. Weiss  
January 8, 1982

Pressure Studies at High and Low Temperatures  
University of Paderborn, Federal Republic of Germany  
G. Piermarini  
February 2, 1982

Current Understanding of Stress-Corrosion Cracking  
Mechanical and Materials Engineering Seminar, Vanderbilt University,  
Nashville, TN  
E. N. Pugh  
February 3, 1982

Chemical Nomenclature: Who Cares and Why?  
American Chemical Society, Wilson Dam Section, Florence, AL  
T. D. Coyle  
March 1982

Environmental Aspects of Organometallic Chemistry  
Chemistry Department, University of Alabama, Birmingham, AL  
T. D. Coyle  
March 1982

Currents in Corrosion Research  
American Chemical Society, Mobile Section, Mobile, AL  
T. D. Coyle  
March 1982

A Rational Function Approximation of Powder Diffraction Profiles  
American Crystallographic Association, Washington, DC  
N. C. Panagiotopoulos and C. R. Hubbard  
March 1982

The Corrosion of Organically Coated Iron and Steel: An Ellipsometric  
Study of the Subcoating Oxide Film Behavior  
Corrosion '82, NACE, Houston, TX  
J. J. Ritter  
March 1982

Inorganic Ion-Doped Glass Beads as Microspectrofluorimetric Standards  
1982 Pittsburgh Analytical Conference, Atlantic City, NJ  
D. K. Hancock, R. A. Velapoldi, J. R. DeVoe, and D. H. Blackburn  
March 9, 1982

High Pressure Phases and Properties  
Howard University, Washington, DC  
S. Block  
March 11, 1982

Characterization of Organometallic Polymers by  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR  
Department of Chemistry, University of Delaware, Newark, DE  
R. B. Johannesen  
March 19, 1982



Aqueous Solutions of Organometals: Implications for Cellular Uptake  
Membrane Bioenergetics Group, Lawrence Berkeley Laboratory, University of California, Berkeley, CA  
F. E. Brinckman  
March 22, 1982

Advances in Speciation of Organometallics and Metal-Containing Macromolecules in Fossil Materials and Process Fluids  
Energy and Environment Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA  
F. E. Brinckman  
March 23, 1982

The Use of Load Pulsing in the Study of Stress-Corrosion Phenomena  
NACE Corrosion Research Conference, Houston, TX  
P. W. Slattery  
March 24, 1982

Pit Initiation and Propagation Rates of 304 Stainless Steel in Chloride Environments  
NACE, Houston, TX  
K. A. Rhyne  
March 24, 1982

Incorporation of Arsenic in Metal-Containing Macromolecules in Shale Oil as Determined by Multielement-Specific Size Exclusion Chromatography  
Symposium on Petroleum Biogeochemistry, 183rd National Meeting  
American Chemical Society, Las Vegas, NV  
C. S. Weiss  
March 29, 1982

Immersion Deposition on Aluminum  
Aluminum Finishing Seminar, St. Louis, MO  
D. S. Lashmore  
March 30, 1982

Analytical Implications of the Signal Collection Process in Laser Enhanced Ionization  
183rd National Meeting, American Chemical Society, Las Vegas, NV  
J. C. Travis, G. J. Havrilla, G. C. Turk, and P. K. Schenck  
March 31, 1982

Preparation of Amorphous Coatings by Coevaporation  
Optical Thin Film Workshop, University of New Mexico, Albuquerque, NM  
D. M. Sanders, E. N. Farabaugh, and W. K. Haller  
April 21, 1982

Development of an NBS Microhardness Standard  
Conference on Microhardness Testing, NBS, Washington, DC  
D. S. Lashmore  
May 1982

Characterization of Slag and Fouling Residues from Co-combustion of Powdered Refuse-derived Fuel with Residual Oil and Comparison with Coal and RDF Residues

Symposium on Resource Recovery from Municipal, Hazardous, and Coal Solid Wastes, Miami, FL

C. R. Robbins and F. Hasselriis

May 1982

Thermodynamic Models of Glass Vaporization

American Ceramic Society, 84th Annual Meeting, Symposium on Glass Modeling, Cincinnati, OH

J. W. Hastie

May 1982

A Comparison of Optical and Mechanical Methods of Thickness Measurement  
Society of Photo-Optical Instrumentation Engineers Technical Symposium, Arlington, VA

A. Feldman and T. Vorburger

May 5, 1982

NMR Examination of Organometallic Copolymers

Naval Biosciences Laboratory, Oakland, CA

R. B. Johannesen

May 5, 1982

A Study of the Underground Corrosion of Copper Concentric Cable

Central Maryland Underground Corrosion Committee Meeting, Baltimore, MD

E. Escalante

May 5, 1982

Ceramic Films by Multi-Source Evaporation

Society of Photo-Optical Instrumentation Engineers Technical Symposium, Arlington, VA

D. M. Sanders, E. N. Farabaugh, and W. K. Haller

May 6, 1982

Development of a Four-Ball Wear Test Procedure to Evaluate Automotive Lubricating Oils

American Society of Lubrication Engineers, Cincinnati, OH

R. G. Gates

May 10-13, 1982

Corrosion Protection Principles and the Development of New Coatings

American Society of Metals SURTECH and SURFACE Coating Exposition, Dearborn, MI

J. Kruger

May 18, 1982

Activity and Phase Equilibria Models in Complex Silicate Systems

CALPHAD XI, Argonne National Laboratories, Chicago, IL

L. P. Cook and J. W. Hastie

May 18, 1982

An Examination of the MCC-1 Leach Test Method, Part III Comparison  
of Glass Composition  
Second Semi-annual Workshop on Leaching Mechanisms of Nuclear Waste  
Forms, Battelle Pacific Northwest Labs., Richland, WA  
D. J. Cronin  
May 19, 1982

Standards for X-ray Powder Diffraction  
X-ray Clinic, State University of New York, Albany, NY  
C. R. Hubbard  
June 1982

Ceramics and Glass Program at NBS  
Refractories Research Center, Ohio State University, Columbus, OH  
T. D. Coyle  
June 1, 1982

Ceramics and Glass Program at NBS  
PPG Industries, Pittsburgh, PA  
T. D. Coyle  
June 2, 1982

Ceramics and Glass Program at NBS  
Alcoa Technical Center, Pittsburgh, PA  
T. D. Coyle  
June 3, 1982

Mass Spectrometric and Thermodynamic Modeling Studies of Glass  
NBS Seminar, Washington, DC  
J. W. Hastie  
June 9, 1982

Characterization of Organometallic Copolymers and Copolymerization  
by Size Exclusion Chromatography  
Sixth International Symposium on Column Liquid Chromatography,  
Cherry Hill, NJ  
E. J. Parks  
June 10, 1982

Mass Spectrometric and Thermodynamic Modeling Studies in Glass  
Saint-Gobain Research Labs., Paris, France  
J. W. Hastie  
June 14, 1982

Further Observations on the Mechanisms of Transgranular Stress-  
Corrosion Cracking  
Sixth Canadian Fracture Conference (Time Dependent Fracture of  
Engineering Materials--Environmental Effects), Vancouver, BC, Canada  
E. N. Pugh  
June 17, 1982

Nuclear Waste Encapsulation  
EG&G, Inc., Idaho International Engineering Lab., Idaho Falls, ID  
R. S. Roth  
June 23, 1982



Transpiration Mass Spectrometry--A New Thermochemical Tool  
NATO Scientific Affairs Division, Thermochemistry School, Viana do  
Castelo, Portugal  
J. W. Hastie  
July 1982

Thermodynamic Modeling of High Temperature Silicate Vaporization  
NATO Scientific Affairs Division, Thermochemistry School, Viana do  
Castelo, Portugal  
J. W. Hastie  
July 1982

Modeling of Silicate Solutions  
Gordon Research Conference on High Temperature Chemistry, Tilton, NH  
J. W. Hastie  
July 1982

High Temperature Chemistry Research at NBS  
Boris Kidrich Institute of Nuclear Physics, Belgrade, Yugoslavia  
J. W. Hastie  
July 1982

Ceramics and Glass Program at NBS  
Sandia National Laboratory, Albuquerque, NM  
S. J. Schneider  
July 1, 1982

$^{13}\text{C}$  and  $^{119}\text{Sn}$  Nuclear Magnetic Resonance  
Workshop on Characterization of Organometallic Polymers, Naval  
Research Laboratory, Washington, DC  
R. B. Johannesen  
July 20, 1982

Tin-Specific Size Exclusion Chromatography  
Workshop on Characterization of Organometallic Polymers, Naval  
Research Laboratory, Washington, DC  
E. J. Parks  
July 20, 1982

Fuel Stability Measurement Methods by Differential Scanning Calorim-  
etry and Thermal Gravimetric Analysis  
CONFAB 82, Saratoga, WY  
S. M. Hsu  
July 21, 1982

Fragmentation Temperature Dependence in Electron Impact Ionization of  
Molecular Beams  
Gordon Research Conference on High Temperature Chemistry, Tilton, NH  
D. W. Bonnell  
July 26, 1982

Electrodeposition of Nickel Chromium Alloys  
Read Conference, University of Pennsylvania, University Park, PA  
D. S. Lashmore  
July 28, 1982

Measurement and Interpretation of Electrochemical Noise  
Gordon Research Conference on Corrosion, New London, NH  
U. Bertocci  
July 30, 1982

XRD Quantitative Phase Analysis Using the NBS Quant 82 System  
Denver X-ray Conference, Denver, CO  
C. R. Robbins, C. R. Hubbard, and R. L. Snyder  
August 1982

X-ray Diffraction Analysis and Particle Size Distribution of Fossil  
Energy Waste Samples  
US DOE Laramie Energy Technology Center, Laramie, WY  
C. R. Robbins  
August 1982

Energy-Dispersive X-ray Microanalysis by the Peak-to-Background Method:  
Empirical Corrections for Detector-Degraded Background Counts  
Electron Microscopy Society of America, Washington, DC  
M. C. Foster, W. A. Hagins, and D. H. Blackburn  
August 11, 1982

The Aqueous Chemistry of Biogenic Organometals  
Gordon Research Conference on Organometallic Chemistry, Andover, NH  
F. E. Brinckman  
August 19, 1982

Pit and Crevice Corrosion of 304 Stainless Steel in Chloride Environ-  
ment as Determined by Electrochemical Techniques  
Nippon Steel Corporation, Kawasaki, Japan  
K. A. Rhyne  
August 27, 1982

Pit and Crevice Corrosion of 304 Stainless Steel in Chloride Environ-  
ment as Determined by Electrochemical Techniques  
Tokoku University, Sendai, Japan  
K. A. Rhyne  
August 30, 1982

Anaerobic Corrosion  
21st Annual Conference of Metallurgists, Toronto, Ontario, Canada  
W. P. Iverson  
September 1, 1982

Defects and Charge Transport in Stabilized  $\alpha$ -Ta<sub>2</sub>O<sub>5</sub>  
Fourth Europhysical Topical Conference on Lattice Defects in Ionic  
Crystals, Trinity College, Dublin, Ireland  
A. E. McHale  
September 2, 1982

HPLC-AA: Keying on Ultratrace Bioactive Molecules by Element Selection  
9th Annual Meeting, Federation of Analytical Chemistry and Spectroscopy  
Societies, Philadelphia, PA  
F. E. Brinckman  
September 22, 1982

## Division Seminars

The Division maintains an active Seminar Program in which lectures by distinguished visitors on scientific topics of interest to the Division are supplemented by presentations of current work by Division scientists. In FY82, the Division sponsored almost three seminars per month, of which two-thirds were presented by scientists from outside NBS.

Recent Studies of Stress-Corrosion Cracking and Liquid-Metal Embrittlement

Stan Lynch

Aeronautical Research Laboratories, Melbourne, Australia

September 30, 1981

Recent NMR Studies of Graphite Intercalation Compounds

Gerald Miller

University of Maryland, College Park, MD

October 22, 1981

Studies by Auger Spectroscopy and Channeling of Si and GaAs Surfaces

Bernard Agius

Institut d'Electronique Fondamentale, Universite Paris XI, France

October 22, 1981

Theoretical and Experimental Studies of Crack Electrochemistry in Structural Steels in a Marine Environment

A. Turnbull

National Physical Laboratory, Teddington, Middlesex, England

October 28, 1981

The Use of Ultramicrotomy in Studying Sections of Filmed and Corroded Surfaces

Graham C. Wood

University of Manchester, Manchester, England

November 3, 1981

The Activities and Operations of the Corrosion and Protection Centre at the University of Manchester Institute of Science and Technology

Graham C. Wood

University of Manchester, Manchester, England

November 3, 1981

Pulsed Electrodeposition of Palladium

J. M. Locarnini

Technisch Chemisches Laboratorium, Swiss Federal Institute of Technology, Zurich, Switzerland

November 6, 1981

Some Measurement Techniques for Fuel Stability Characterization

A. L. Cummings, P. Pei, and S. M. Hsu

National Bureau of Standards, Gaithersburg, MD

November 20, 1981



Program of the Structural Chemistry Group  
S. Block, G. J. Piermarini, F. A. Mauer, and R. G. Munro  
National Bureau of Standards, Gaithersburg, MD  
November 24, 1981

Some Effects of Oxidation on the Wear Behavior of Base Stocks and Additives

P. A. Willermet  
Ford Motor Company, Dearborn, MI  
December 4, 1981

Current Research in the Chemical and Biodegradation Processes Group  
F. E. Brinckman, R. B. Johannesen, and G. J. Olson  
National Bureau of Standards, Gaithersburg, MD  
December 17, 1981

Characterization of Surface Properties of Importance in Tribology  
Donald Buckley  
National Aeronautics and Space Administration, Lewis Research Center,  
Cleveland, OH  
January 7, 1982

Activities of the Glass and Optical Materials Group  
W. K. Haller, M. J. Cellarosi, D. H. Blackburn, D. J. Cronin,  
E. R. Farabuagh, A. Feldman, and D. H. Sanders  
National Bureau of Standards, Gaithersburg, MD  
January 25, 1982

Determination of Molecular Constants by Matrix Isolation NMR Spectroscopy  
Kurt W. Zilm  
University of Utah Research Center, Salt Lake City, UT  
February 9, 1982

Experimental and Theoretical Computational Activities in Phase Equilibria of Ceramic Systems  
R. S. Roth, L. P. Cook, and A. McHale  
National Bureau of Standards, Gaithersburg, MD  
February 11, 1982

Vapor Pressure Measurement Above Nuclear Fuels at 5000 to 7000 K  
J. F. Babelot  
Karlsruhe Establishment, Europa Institute for Transuranium Elements,  
Federal Republic of Germany  
March 19, 1982

A-C Anodizing of Aluminum  
Joseph Zahavi  
Israel Institute of Metals, Technion City, Haifa, Israel  
April 12, 1982

Current Research in Corrosion Group  
J. Kruger, U. Bertocci, E. Escalante, V. K. Hardman, E. N. Pugh, and  
J. J. Ritter  
National Bureau of Standards, Gaithersburg, MD  
April 13, 1982

Corrosion Problems in Ethanol Fuel Powered Cars  
Deniol K. Tanaka  
Instituto de Pesquisas Tecnológicas, Sao Paulo, Brazil  
April 20, 1982

Activities of the Ceramic Processing and Durability Group  
T. Negas  
National Bureau of Standards, Gaithersburg, MD  
April 29, 1982

Stress Corrosion Cracking of Mg Alloys  
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### Sponsored Conferences

Sixth Annual Conference on Materials for Coal Conversion and Utilization  
Department of Energy, Electric Power Research Institute, Gas Research  
Institute, and National Bureau of Standards  
S. J. Schneider, Chairman  
October 7-9, 1981

American Crystallographic Association  
National Bureau of Standards/Smithsonian Institution  
C. R. Hubbard and J. K. Stalick, Co-chairpersons  
March 29-April 2, 1982

Symposium on Environment-Sensitive Fracture: Evaluation and  
Comparison of Test Methods  
American Society for Testing and Materials/National Bureau of Standards  
E. Neville Pugh and G. M. Ugiansky, Co-chairmen  
April 26-28, 1982

Gordon Research Conference on Corrosion  
E. Neville Pugh, Chairman  
July 26-30, 1982

#### Standard Reference Materials

SRM 640a - 2 $\theta$ /D-spacing Standard for X-ray Diffraction  
C. R. Hubbard, 1982

SRM 774 - Glass Dielectric Constant and Loss Characteristic  
M. J. Cellarosi, 1982

#### External Recognition

G. J. Olson  
Visiting Scientist, Department of Biology, Washington University,  
St. Louis, MO  
January 1982

F. E. Brinckman  
Guest Worker, Lawrence Berkeley Laboratory, University of California,  
Berkeley, CA  
March 1982

C. S. Weiss  
Guest Scientist, Department of Chemistry, Texas A & M University,  
College Station, TX  
April 1982

#### Patents

Fluidic Thermistor/Fugacity Device  
T. Negas, L. P. Domingues, T. M. Drzewiecki, and R. M. Phillippi  
Patent No. 4,264,423,  
April 28, 1981

## Industrial Interactions

### 1. INDUSTRIAL RESEARCH ASSOCIATES

#### Electrodeposition Group--David S. Lashmore, Group Leader

- The Aluminum Association and American Electroplaters Society: David Thomas--Research Associate, sponsor: David S. Lashmore. The program is set up to investigate electrodeposition of anodized aluminum.

#### Ceramic Sciences Group--Taki Negas, Group Leader

- Joint Committee for X-ray Powder Diffraction Standards (JCPDS)--International Centre for Diffraction Data. Staff at NBS: M. E. Morris--Director, E. H. Evans, N. Pyros, Research Associate, B. Paretzkin, H. F. McMurdie, H. S. Parker, D. Gladhill, S. Lederman, C. Wingo; B. Snyder--consultant, Alfred Univ., Dept. Ceramic Engineering, sponsor: C. R. Hubbard and T. Negas.

This non-profit corporation functions in cooperation with the American Ceramic Society, the American Crystallographic Association, the American Society for Testing and Materials, the Clay Minerals Society, the Institute of Physics, the Mineralogical Society of America, the Mineralogical Society of Great Britain and Ireland, the National Association of Corrosion Engineers, and the Societe Francaise de Mineralogie et de Cristallographie. JCPDS produces the Powder Diffraction File (PDF) which is a continuing compilation of diffraction patterns gathered from numerous sources. Over 80 industries in Fortune 500 and over 1200 other private, government, and academic organizations purchase the data. NBS contributes new or improved data to the PDF as well as XRD techniques and SRMs especially applicable to the processing and quality control of ceramic and metal alloy materials.

#### Chemical and Biodegradation Processes Group--Frederick E. Brinckman, Group Leader

- Mobil Research and Development Corporation; Research Associate: Thomas F. Degnan; NBS Sponsor: Frederick E. Brinckman--molecular characterization and monitoring of arsenic catalyst poisons in candidate processes for shale oils-measurement technology.

#### Glass and Optical Materials Group--Wolfgang K. Haller, Group Leader

- Approximately 20 glass companies through ASTM; Sponsor Research Associate: Dr. A. C. Siefert. NBS sponsors: G. A. Urano and M. J. Cellarosi. The program establishes priority listing of SRMs of interest to glass industry and coordinates SRM-material procurements and work done outside of NBS.



### Tribochemistry Group--Stephen M. Hsu, Group Leader

- Chinese Petroleum Corporation; Ron Lin and S. M. Hsu. The program characterizes lubricant composition with respect to oxidation stability and wear-measurement technology.

## 2. OTHER INDUSTRIAL GUEST WORKERS AT CMS

### High Temperature Processes Group--John W. Hastie, Group Leader

- Robert J. Cava, Bell Labs, Murray Hill, NJ.  
NBS sponsor: Robert S. Roth  
This work deals with neutron diffraction of ionic conductivity materials.

### Ceramic Sciences Group--Taki Negas, Group Leader

- T. M. Drzewiecki, Systems Planning Corporation, VA  
NBS sponsor: T. Negas  
The work of this program determines durability of ceramic coatings on metals in molten metal (800-1550 °C) environments.
- L. P. Domingues, Research and Development Director, Trans-Tech, Inc., MD  
NBS sponsor: T. Negas  
The work deals with the characterization of ceramic powders, green compacts, and densified microstructures for technical ceramics.

## 3. ARCHIVAL TECHNICAL PAPERS CO-AUTHORED WITH INDUSTRIAL EMPLOYEE

### Corrosion Group--Jerome Kruger, Group Leader

- "Studies of Hydrogen Embrittlement and Stress-corrosion Cracking in an Aluminum-Zinc-Magnesium Alloy" by:  
E. N. Pugh, NBS; S. W. Ciariardi, Amoco; J. L. Nelson, INCO;  
R. A. Yeske, Westinghouse, Hydrogen Effects in Metals, TMS-AIME (1981), p. 437.
- "A Comparison of Gaseous Hydrogen Embrittlement, Slow-strain-rate Hydrogen Embrittlement, and Stress-corrosion Cracking in Ti-8Al-1Mo-1V" by:  
E. N. Pugh, NBS; G. H. Kock, Battelle; R. Liu, Bell Labs. Met. Trans. A., 12A, 1833 (1981).
- "On the Mechanism of SCC in Mg-Al Alloy" by:  
E. N. Pugh, NBS; D. G. Chakrapahi, Mei-Charlton, Inc. Proc. 6th Internat. Congress on Metallic Corrosion, in press.
- "Recent Observations on the Propagation of Stress-corrosion Cracks and Their Relevance to Proposed Mechanisms of SCC" by:  
E. N. Pugh, NBS; D. V. Beggs, Conoco. Proc. of A. R. Troiano Honorary Symposium on Hydrogen Embrittlement and SCC, in press.

High Temperature Processes Group--John W. Hastie, Group Leader

- "The Structure of  $\text{LaTaO}_4$  at 300 °C by Neutron Powder Profile Analysis" by:  
R. S. Roth, NBS; R. J. Cava, Bell Labs.  
J. Solid State Chem., 36 139 (1981)
- "Crystal Chemistry, Modulated Structure, and Electrical Conductivity in the Oxygen Excess Scheelite Based Compounds  $\text{La}_{1-x}\text{Th}_x\text{NbO}_{4+x/2}$  and  $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+x/2}$ " by:  
R. S. Roth, NBS; T. Negas, NBS, R. J. Cava, Bell Labs.;  
H. S. Parker and D. B. Minor.  
J. Solid State Chem., 40, 318 (1981)
- "Revised  $\text{ThO}_2\text{-Nb}_2\text{O}_5$  Phase Diagram" by:  
R. J. Cava, Bell Labs; R. S. Roth, NBS; D. B. Minor  
J. Am. Ceram. Soc. Comm. 64, p. C64, April 1981
- "Structural Aspects of Lithium Insertion in Oxides:  $\text{Li}_x\text{ReO}_3$  and  $\text{Li}_2\text{FeV}_3\text{O}_8$ " by:  
R. J. Cava, Bell Labs; A. Santoro, D. W. Murphy, S. Zahurak,  
and R. S. Roth, NBS.  
Solid State Ionics 5, 323 (1981)
- "Use of the Pearson Type VII Distribution in the Neutron Profile Refinement of the Structures of  $\text{LiReO}_3$  and  $\text{Li}_2\text{ReO}_3$ " by:  
A. Santoro, R. J. Cava, Bell Labs; D. W. Murphy and R. S. Roth, NBS.  
Acta Crystallogr., in press
- "The Structures of Lithium Inserted Metal Oxides:  $\text{LiReO}_3$  and  $\text{Li}_2\text{ReO}_3$ " by:  
R. J. Cava, Bell Labs; A. Santoro, D. W. Murphy, S. Zahurak,  
and R. S. Roth, NBS.  
J. Solid State Chem., 42, 251 (1982)
- " $\text{FeNb}_3\text{Se}_{10}$ : A New Structure Type Related to  $\text{NbSe}_3$ " by:  
R. J. Cava, Bell Labs; V. L. Himes, A. D. Mighell, and R. S. Roth, NBS.  
Phys. Rev. B, 24, No. 6, Sept. 15, 1981.

Ceramic Sciences Group--Taki Negas, Group Leader

- "Design of Fluidic Capillary Pyrometer for Contact Duty at Temperatures to 2750 °C", Symposium (VI) on Temperature, June 1982. T. Negas, NBS; T. M. Drzewiecki, Systems Planning Corp.; R. M. Phillippi, U.S. Army (guest worker with T. Negas).
- "Fabrication, Testing, and Evaluation of Prototype Fluidic Capillary Pyrometer Systems", Journal of Dynamics Systems and Control, ASME, December 1981. T. Negas, NBS; R. M. Phillippi, U.S. Army; T. M. Drzewiecki, Systems Planning Corp.; L. P. Domingues, Trans-Tech (guest worker with T. Negas).
- "Fabrication of Ceramic Fluidic Capillary Temperature Sensors" (in press) by:  
T. Negas, NBS; L. P. Domingues, Trans-Tech; R. D. Amren, Trans-Tech; R. M. Phillippi, U.S. Army; T. M. Drzewiecki, Systems Planning Corp.

- "Crystal Chemistry, Modulated Structure, and Electrical Conductivity in the Oxygen Excess Scheelite-based Compounds  $\text{La}_{1-x}\text{Th}_x\text{NbO}_{4+x/2}$  and  $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+x/2}$ " (in press), J. Solid State Chem., 40(3) December 1981. R. S. Roth, NBS; T. Negas, NBS; R. J. Cava, Bell Labs.
- "Preparation of High-Density Ceria-Yttria Ceramics" by: A. L. Dragoo, NBS; L. P. Domingues, Trans-Tech, J. Am. Ceram. Soc., 65(5) May 1982.
- "NBS Monograph 25-Section 18, Standard, X-ray Diffraction Powder Patterns" U.S. Dept. of Commerce/NBS, October 1981 Section 19, October 1982, by: C. R. Hubbard, NBS; JCPDS staff.
- "Characterization of Ash Residues From a Refuse-Derived Fuel/Oil Combustion Study," ASTM Symposium on Alternative Fuels and Future Fuel Specifications for Stationary Gas Turbine Applications, by: C. R. Robbins, NBS; F. Hasselriis, Combustion Equipment Associates.
- "Characterization of Slag and Fouling Residues from Co-Combustion of Powdered Refuse-Derived Fuel with Residual Oil and Comparison with Coal and RDF Residues", accepted for publication, by: C. R. Robbins, NBS; F. Hasselriis, Combustion Equipment Associates.

#### Tribochemistry Group--Stephen M. Hsu, Group Leader

- "Base Oil Composition Effects on Oxidation Stability," S. M. Hsu and C. S. Ku, R. Lin, Chinese Petroleum Corporation.

#### 4. FORMAL VISITS (FY81 through FY82)

#### Corrosion Group--Jerome Kruger, Group Leader

#### Visits to NBS

- Owens Corning, April 12, 1982--corrosion of metals protected by coatings.
- INCO, July 6, 1982--stress-corrosion test methods.
- EPRI, December 5, 1980--underground corrosion of power cables.
- Battelle, October 24, 1980--approaches toward the estimation of corrosion rates of nuclear waste canisters.
- Texas Instruments, October 28, 1980--underground corrosion of telephone cables.
- Texas Instruments, May 21, 1982--possibilities for establishing a corrosion data center at NBS.
- Concrete Pipe Association, February 19, 1982--possibility of a CPA research associateship on corrosion of aluminum in soils.
- Bethlehem Steel Corp., January 16, 1981--piling corrosion.
- U. S. Steel Corp., January 16, 1981--piling corrosion.
- American Iron and Steel Inst., January 16, 1981--piling corrosion.
- Cathodic Protection Consultants, March 11, 1981--corrosion in concrete.
- Florida Power and Light Co., April 22, 23, 1981--corrosion of electric power cable.



- Armstrong Products Co., May 27, 1981--protection of piling.
- Baltimore Gas and Electric, June 3, 1981--corrosion of concrete.
- U. S. Steel Corp., June 26, 1981--corrosion of piling.
- Bethlehem Steel, November 4, 1981--corrosion of piling.
- U.S. Steel, November 4, 1981--corrosion of piling.
- Baltimore Gas and Electric, June 17, 1982--corrosion of electric power cable.
- Federated Metals (ASARCO), December 1, 1981--protection of electric power cable.

#### Visits by NBS

- Electrical Power Research Inst., April 29, 1981--corrosion of electric power cable.
- Baltimore Gas and Electric Power, May 22, 1981--corrosion of electric power cable.
- Charles R. Velzy Assoc., June 3, 1981--Corrosion in incinerators.
- MCP Facilities, Inc., September 25, 1981--protection of piling.

#### Electrodeposition Group--David S. Lashmore, Group Leader

#### Visits by NBS

- David Craig, Ford Motor Company, May 28, 1982--wants our Group to produce electrochemical type thickness standards.
- John Dueber, Degussa Corp., American Electroplaters Society, May 27, 1982--get acquainted with our work on plating nickel-chromium alloys.
- Takeyuki Fukuda, Nippon Steel Corp., June 1, 1982--information on our dye penetrant test SRMs.
- Richard Sard, Utillyte Chemical Corp., July 1982--information on deposition of metallic glass alloys.
- Vasanth Kunigamalli, Goddard Space Flight Center, May 1982--become acquainted with work done by Group, especially alloy plating and black coatings.
- Yair Assaf, Bokak Electroplaters Co. LTD., Israel--information on pulsed electrodeposition.
- James McGuire, Pres., Applied Systems, Inc., McLean, VA., January 1981--information on black electroless nickel for night vision devices.
- Frank Brown, Eastman Kodak, May 1981--information on black electroless nickel for technical group on radiometry.
- Members of ASTM Committee E-44 (Solar Conversion), March 1981--information on black electroless nickel for solar energy conversion applications.
- Members of ASTM Committee E-21 (Space Simulation), October 1981--information on black electroless nickel for application in space simulation.
- Fred Roselle, Westinghouse, December 1981--information on black electroless nickel for application for image intensifiers in video cameras for night surveillance for industry and military.
- John Caulfield, Arthur D. Little Co., June 1981--applications for black electroless nickel for solar energy.

- Ball Aerospace, Boulder, CO--recipients of patent rights for black electroless nickel.

Chemical and Biodegradation Processes Group--Frederick E. Brinckman, Group Leader

Visits to NBS

- A. Fetell and J. Reardon, E. I. DuPont and Nemours Company, May 8, 1981--discuss design and commercial production of "tailored" organotin polymers meeting Navy service criteria as controlled-release marine antifouling paints.
- Bernard Tramier, Societe Nationale Elf Aquitaine, France, June 18, 1982--measurement methodology for monitoring industrial organotin biocide uses and applications of FT-NMR to in situ characterization of heteroatomic molecules in petroleum refining.
- J. Truella and C. Simpson, Mobil Research and Development Corp., July 22, 1982--applications of multi-nuclear FT-NMR to syncrude processing measurements and use of element-specific chromatographic detectors for refractory metal molecular speciation in syncrude processing catalysts.

Visits by NBS

- F. E. Brinckman, M and T Chemicals, Inc., June 8, 1982--consult with senior management on measurement problems associated with recent oyster kills in France and ban on organotin use there.
- F. E. Brinckman and R. B. Johannesen, Rohm and Haas Co. and Monsanto Chemical Co., July 20, 1982--at request of Navy sponsor consult with industrial contractors on current status of measurement and production problems with large-scale procurement of fleet antifoulant organotin polymers (at Naval Research Lab).

High Temperature Processes Group--John W. Hastie, Group Leader

Visits by NBS

- R. T. Frost, General Electric Space Laboratories, May 1982--discuss levitation calorimetry.

Ceramic Sciences Group--Taki Negas, Group Leader

Visits to NBS

- Nutan C. Bhiwandker, Hameed Khan and J. Bedgood, Ampex Corporation, CA, May 1982--tour facilities and discuss extrusion of lithium ferrite wave guides.
- T. Gluckner and B. Cottage, Progressive Apparel, VA, July 1982--discuss sintering of SiC and SiC composites (visited once a week from July 1982 on).
- J. Shade, Battelle Pacific NW Labs., May 1982--tour facilities and discuss ceramic processing of nuclear waste.

- R. M. Arons, and O. R. Hughes, Celanese Research Company, April 1982--discuss advances in ceramic powder processing for potential marketing.
- J. Werth, Englehard Industries, November 1981--discuss ceramic coatings for fuel cell applications.
- Delegation from Carborundum Corp. (through S. J. Schneider)--discuss corrosion problems with  $ZrSiO_4$ -based, fusion cast refractories.
- E. Demaray, Airco Temescal, April 1982--discuss zirconia powders for turbine coatings.
- V. E. Haloulakos, McDonnell Douglas Astronautics Company, CA, June 1982--discuss ceramic coatings for refractory metals.
- Delegation from Japanese Steel/Ceramics Industries--ceramic sensors for temperature measurements.
- Corning Group (through J. B. Wachtman)--ceramic sensors and fabrication.
- D. Harris, APS Materials, Inc., OH, September 1981--plasma spray ceramic powders and technology, potential joint effort with NBS and NASA.
- A. Morrell, Thomson-CSF, France, April 1982--processing of microwave ceramics.
- J. Skalny, Martin Marietta Labs, MD, June 1982--characterization and classification of coal ash.

#### Visits by NBS

- AiResearch Company, Garrett Corporation, CA, June 30, 1982--industrial needs for ceramic research.
- Ampex Corp., CA, June 28, 1982--industrial needs for ceramic research.
- Rockwell International Science Center, CA, June 29, 1981--industrial needs for ceramic research.
- Martin Marietta Laboratories, MD, May 19, 1982--industrial needs for ceramic research.
- Harbison-Walker Refractories, Co., PA, June 2, 1982--industrial needs for ceramic research.
- PPG Industries, PA, June 2, 1982--industrial needs for ceramic research.
- Alcoa Technical Center, PA, June 3, 1982--industrial needs for ceramic research.
- Westinghouse Research and Development Center, PA, June 4, 1982--industrial needs for ceramic research.
- Walmet Division, GTE--industrial needs for ceramic research in cemented carbides.

#### Glass and Optical Materials Group--Wolfgang K. Haller, Group Leader

#### Visits to NBS

- Airco-Temescal, Fall 1981--zirconia films-glassy film evaporation work.



- Balzers, May 1982--NBS glassy film process.
- Optical Coatings Lab (OCLI), Fall 1981--NBS glassy film process.
- Sperry-Rand UNIVAC, February 1982--metallized glass fibers for electronic circuit-boards.
- Brockway Glass Co., February 1982--NBS glass melt evaporation work.
- Dentsply International, Fall 1981--fluorescence in artificial teeth.
- COMSAT, several times--structure of silica.
- Shell Development Corp., Fall 1981--coal slag viscosity.
- Tracor, Winter 1981/82--optical properties for fiber optic material.
- Owens-Corning Fiberglas, December 1981--fiberglass reinforced portland cement materials.
- Owens-Corning Fiberglas, Fall 1981--glass evaporation studies of NBS.

#### Visits by NBS

- Martin Marietta--to assess industrial needs in glass.
- Ampex Corporation--to assess industrial needs in glass.
- Hoya-USA--to assess industrial needs in glass.

#### Tribochemistry Group--Stephen M. Hsu, Group Leader

#### Visits to NBS

- Geo Centers Inc., November 5, 1980--to characterize of deuterated hydrocarbons.
- Mobil Research and Development, November 10, 1980--to plan for the NBS/ASTM cooperative study.
- Idemitsu Oil Company, January 16, 1981--friction and wear test methods.
- Mobil Oil, January 16, 1981--base oil characterization methods.
- Texaco, January 21, 1981--characterization of lubricating base oils.
- Amoco, February 4, 1981--Amoco-NBS cooperation on bench test development.
- Mobil, July 20, 1981--base oil consistency program.
- Amoco, January 21, 1982--oxygen uptake test methodology.
- Mobil, January 15, 1982--Tribology programs at NBS.
- Chinese Petroleum Institute, March 10, 1982--lubricant research.
- Mobil, July 8, 1982--NBS-industry cooperative study program planning.
- Lubrizol, July 8, 1982--NBS-industry cooperative study program planning.
- Shell (Canada), July 8, 1982--NBS-industry cooperative study program planning.
- Gulf, July 8, 1982--NBS-industry cooperative study program planning.
- Exxon, July 8, 1982--NBS-industry cooperative study program planning.
- Paramins, July 8, 1982--NBS-industry cooperative study program planning.
- Imperial Oil (Canada), July 8, 1982--NBS-industry cooperative study program planning.

- Ciby Geigy, July 8, 1982--NBS-industry cooperative study program planning.
- Sun Oil, July 8, 1982--NBS-industry cooperative study program planning.

#### Visits by NBS

- Gulf Oil, October 13, 1980--talk on research needs in lubrication.
- Gulf Oil, October 30-31, 1980--information exchange on various technical projects.
- Imperial Oil, September 16, 17, 1981--discuss various technical topics in base oil characterization research and agreed to cooperate.
- API, February 4, 1982--discuss mutual interest in petroleum research.
- Lubrizol, August 26, 1982--discuss technical information exchange and possible cooperative programs.

### 5. PARTICIPATION IN MEASUREMENT PROGRAMS

#### Corrosion Group--Jerome Kruger, Group Leader

- ASTM G01.06.02--Stress Corrosion Test Environment, round robin on chloride stress corrosion cracking.
- ASTM G01.10--Corrosion in Soils, round robin on corrosion measurements in soils.

#### Electrodeposition Group--David S. Lashmore, Group Leader

- ASTM B08--round robin beta-backscatter (coating thickness measurements).

#### Chemical and Biodegradation Processes Group--Frederick E. Brinckman, Group Leader

- ASTM G-1--Corrosion of Metals, W. P. Iverson participated in round robin test comparing electrochemical corrosion measurement methods.

#### High Temperature Processes Group--John W. Hastie, Group Leader

- DuPont Savannah River Laboratory--vaporization of simulated nuclear waste glass materials, DuPont prepares samples and provides applied data from pilot plant experience and we provide high precision basic data on vaporization rates needed for optimizing plant conditions for minimization of vaporization losses.
- DOE-Morgantown, G.E., Westinghouse, and other gas turbine and air pollution control companies--collaborative program, participants provide pilot plant experiences and manufacture alkali emission control devices, we provide basic thermochemical data on alkali vapor transport from materials present in combustor such as coal ash/slag, dolomite, and glass or ceramic alkali absorbants.

- NBS, GE, Rice University (NASA support)--joint program, experiment on levitation calorimetry of liquid tungsten, experiments designed by us and carried out at GE, King of Prussia, PA laboratories.

#### Ceramic Sciences Group--Taki Negas, Group Leader

- Exxon Production Research Co., Texas--round robin, "Comparison of Mineral Constituents in a Sample From Herrin (No. 6) Coal Member From Illinois," to be published in a USGS Survey Circular (~ 1983), Dr. R. B. Finkelman, editor.

#### Glass and Optical Measurements Group--Wolfgang K. Haller, Group Leader

- ASTM--round robins and interlaboratory testing programs on (a) Electrical high temperature resistivity of glass melts, (b) Dielectric constant of glass (SRM), (c) Thermal expansion of glass, (d) Analysis of high alumina sand, (e) Analysis of ferrous/ferric ratio of glasses. Involves: Owens-Corning Fiberglas, Owens-Illinois Glass Company, Anchor Hocking Glass Company, Johns-Manville Company, Corning Glass Company, Brockway Glass Company, Ferro Corporation, General Electric, PPG Industries, LOF Company, AFG Industries.

#### Tribochemistry Group--Stephen M. Hsu, Group Leader

- NBS/ASTM Basestock Consistency Program. The program involves taking monthly production samples from 10 refineries (four virgin oil refineries, six re-refineries) and the samples are measured by 14 participating labs for quality and consistency. Each lab conducted different tests (about 40 tests on each sample). Results were sent to NBS for analysis and compilation. Companies participating include: Mobil, Shell, Lubrizol, Gulf, Chevron, Filmit Oil, Motor Oil Refining Company, Savant, Texaco, Sun.
- NBS sponsored base oil research program. This program aims at understanding the base oil compositional effects on oxidation stability. Over 100 base oil samples from 14 different crude sources were collected. Each company also furnishes compositional and other analytical data on each sample. Companies participating include: Lubrizol, Amoco, Shell (Canada), Gulf, Chevron, Mobil, Exxon, Paramins, Imperial (Canada), Sun.

### 6. DATA PROGRAMS

#### Corrosion Group--Jerome Kruger, Group Leader

- EPRI--research on underground corrosion of copper concentric neutrals on power cables.
- AISI--corrosion data on corrosion of piling.
- AISI--corrosion data on underground corrosion of stainless steels.



High Temperature Processes Group--John W. Hastie, Group Leader

- American Ceramic Society Advisory Committee on Phase Equilibria Data Center--Lawrence P. Cook, chairman.
- American Ceramic Society, Development Committee, S. J. Schneider.

Ceramic Sciences Group--Taki Negas, Group Leader

- JCPDS--round robin, "Comparison of Mineral Constituents in a Sample From Herrin (No. 6) Coal Member From Illinois", to be published in a USGS Survey Circular.
- Materials and Components for Fossil Energy Applications, H. M. Ondik and A. Perloff, performance and property evaluated data for ceramics, alloys, composites. Industrial contractors' reports through DOE utilized predominately as data source. Publication of "Construction Materials for Coal Conversion" anticipated in 1983.

Electrodeposition Group--David S. Lashmore, Group Leader

- ASTM round robin on microhardness (B08).
- ASTM round robin on beta-backscatter instruments.

7. FORMAL ADVISORY ACTIVITIES

Corrosion Group--Jerome Kruger, Group Leader

- Metals Properties Council--Subcommittee and Task Group on Corrosion Fatigue Testing.
- EPRI--Corrosion Advisory Committee on Nuclear Reactors.
- Metals Properties Council--Subcommittee and Task Group on Corrosion of Metals in Association with Concrete.

Electrodeposition Group--David S. Lashmore, Group Leader

- National Materials Policy Board--David Lashmore is NBS representative on Flame Sprayed Coatings.

Chemical and Biodegradation Processes Group--Frederick E. Brinckman, Group Leader

- Chemical Manufacturers Association--F. E. Brinckman organized CMA-sponsored Symposium on Arsenic Production and Use, NBS, November 4-6, 1981.
- International Tin Research Institute (U.K.), F. E. Brinckman--consultations on development of organotin speciation standard for industry.
- International Biodeterioration Research Group, U.S., W. P. Iverson--surveyed current research in field, evaluated most important industrial problems in field with recommendations for future research.

- International Nutritional Anemia Consultative Group--The Nutritional Foundation, Inc., F. E. Brinckman--invited consultant on matters dealing with measurements of bioavailability of iron and its compounds commercially added to foodstuffs, food industry-wide sponsorship.

Ceramic Sciences Group--Taki Negas, Group Leader

- JCPDS Board of Directors, C. R. Hubbard, Vice-chairman and technical coordinator at NBS.
- American Ceramic Society, T. Negas, L. P. Cook, and R. S. Roth--Co-editors, Phase Diagrams for Ceramists.
- Materials Review Board (MRB), T. Negas--for data and procedures related to nuclear waste materials and testing by the Materials Characterization Center, Battelle NW; industry to utilize data for encapsulation and disposal of nuclear wastes.





## FRACTURE AND DEFORMATION DIVISION (562)

Richard P. Reed, Chief  
Sheldon M. Wiederhorn, Deputy Chief  
C. Montgomery, Secretary

Structures and components must be mechanically reliable. A significantly large portion of our Nation's effort to ensure public safety and environmental quality concentrates on material and structural mechanical integrity. Material fracture imposes a high cost on the national economy. Careful design, structural codes and standards, material development and characterization, quality control and inspection, and the replacement, inconvenience, injuries, and deaths from unexpected failures all contribute to this cost.

The Division has completed assessment of the costs of fracture to the Nation. The results are being reported to the Subcommittees on Natural Resources and Environment and on Science, Research, and Technology of the House of Representatives Committee on Science and Technology. Even with the use of the currently best available design, fabrication, and inspection procedures, sometimes structures, mechanical components, and containers fail during use. The economic consequences for the domestic economy of unintended failures and the costs to prevent fracture have been found to be large, of the order of 4 percent of the Gross National Product. The economic benefits to be derived from wider application of existing fracture-control technology have been determined. The economic impact of generic research to improve understanding of fracture processes and to control fracture have been estimated. Various research areas to facilitate future cost reductions have been identified.

Division personnel are located in both Boulder and Gaithersburg. Although separate geographically, these two groups complement each other. The Boulder group emphasizes elastic-plastic fracture mechanics and low-temperature properties in its study of metals, alloys, and composites. The Gaithersburg group emphasizes time-dependent deformation and fracture mechanisms, high-temperature properties of metals and alloys, and mechanical properties of ceramics. Together these groups represent most of the expertise in mechanical properties and in fracture mechanics at NBS.

The technical outputs of the Division assist many Government agencies, especially the Departments of Energy, Transportation, Defense and Interior. Recent emphasis on fusion, coal conversion, off-shore drilling and geothermal energy has led to several efforts: low-temperature research for structural containment of the large magnetic fields produced by superconducting magnets, property characterization of geothermal cements, study of high-temperature deformation and crack growth of coal-conversion-system structural ceramics, the preparation of a handbook on coal-conversion-system material performance. Transportation-related research includes: research to establish inspection and allowable-flaw-size standards for pipeline girth welds, mechanical-property and microstructural characterization of pressure-tank-car steels and railroad wheels, fracture-mechanics assessment of tank-car behavior, development of test

standards for lightweight compressed gas cylinders, and numerous structural metal-fracture analyses. Research for the Department of Defense is diverse. We are assisting in upgrading Navy fracture-control plans, identifying micro-creep limitations in ultrasensitive inertial-guidance-system gyroscopes, studying the applicability of proof testing to nitride and carbide ceramics that may be used in gas-turbine engines, conducting erosion and wear experiments of ceramics to reduce machining costs, studying the fracture and elastic characteristics of new silicon-carbide, aluminum-based composites, and conducting large-scale panel tests on high-strength low-alloy steels.

The Division hosts and leads a number of workshops and conferences each year. Collaborating with the Department of Energy (DOE), annual workshops on "Materials at Low Temperatures" are hosted each year. The Mechanical Failures Prevention Group, supported by the Division, hosted two conferences: "Damage Prevention in the Transportation Environment" and "Time-Dependent Failure Mechanisms and Assessment Methodologies." This past year with the Office of Naval Research the Division hosted a workshop on "Contact Damage in Ceramic Materials at Elevated Temperature." The Division actively leads and supports the International Cryogenic Materials Conference, which will hold its next meeting in Colorado Springs, CO.

New emphasis has been placed on non-destructive evaluation and characterization. Experienced scientists have been added to the Division in Gaithersburg to initiate research in eddy-current scattering theory, laser-based remote ultrasonic detection of flaws and acoustic emission imaging and mapping. In Boulder, the research in theoretical modeling and development of electromagnetic acoustic transducers has been expanded from defect characterization to residual stress measurements.

The principal goal of the Fracture and Deformation Division is to minimize material failure. There are three essential generic research thrusts to improve material mechanical performance:

1. Theory and modeling of deformation and fracture lead to a fundamental understanding of the mechanisms of material mechanical response.
2. Characterization of mechanical performance is essential for the proper development and selection of materials for service applications and for efficient design that takes full advantage of the performance.
3. Fracture-mechanics development and application provide quantitative assessment and standards for the integrity of critical structures by relating material properties to flaw characterization and service environment.

The Fracture and Deformation Division focuses on long term research emphasizing the critical areas of these three thrusts. These critical areas, subsequently referred to as Tasks, are considered high risk and are discussed in this report. Three principal research tasks have been established to emphasize the research directions of our Division:



12121 FRACTURE MECHANISMS AND ANALYSES. Many advancing technologies are restricted by the lack of understanding of time-dependent deformation and fracture mechanisms. Failure analyses to assist in understanding the causes of major national structural catastrophies are also included in this task.

12122 DURABILITY OF CERAMICS AND COMPOSITES. Two areas of rapidly advancing material utilization are composites and ceramics. Uses of both material classes are primarily restricted by mechanical performance.

12123 ELASTIC-PLASTIC FRACTURE MECHANICS. The development of elastic-plastic fracture mechanics will provide the opportunity to apply quantitative fitness-for-service criteria to the codes and standards of critical structures.

#### FY82 Significant Accomplishments

Task 12121--FRACTURE MECHANISMS AND ANALYSES. Our program on fracture mechanisms and failure analyses has as its objectives a broad spectrum of goals: (1) the development of fundamental theories on crack-tip structures and processes, (2) the generation of data to elucidate these crack-tip mechanisms, (3) the development of fracture methodologies for predicting structural reliability, and (4) the application of established methodologies in the analysis of actual failures. In addition, the NBS Materials Durability Program has provided funding for increased emphasis on high-temperature fracture processes and mechanisms. Our understanding of the fracture of metals under time-dependent conditions will be increased by research on crack-tip theory coupled with high-temperature tensile, creep, and fatigue properties.

- A generalized defect Green's function formalism was developed for treating a crack as a crystalline defect. Decomposition of the solution into a linear-elastic lattice solution and a nonlinear crack-tip core solution allows details of the crack-tip cohesive interaction and of chemically assisted bond rupture to be examined.
- Stability criteria of a sharp crack against intrinsic ductile blunting by dislocation emission were examined with respect to dislocation interactions in multiple emission events and the prospects for combined cleavage and dislocation emission.
- Models have been developed to calculate the enhanced toughness of ductile materials due to plasticity shielding of the crack-tip stress field. Continuum calculations have been augmented by discrete dislocation models with an essential feature of these models being an elastic enclave, or dislocation-free zone, ahead of the crack tip.
- A plastic yield strip model has been used to analyze a variety of fracture related situations. When used to study residual strength diagrams (a plot of failure stress versus crack size



for a cracked structure), the model demonstrates that the usual categories of linear-elastic and elastic-plastic fracture mechanics lose their distinction. The model has also been successfully applied in the ASTM "Predictive Round Robin on Fracture" sponsored by Task Group E24.06.02.

- Diffusive mechanisms of cavity growth along grain interfaces at elevated temperatures were examined in terms of the coupled effects of elastic deformation and atomic diffusion. Three regimes of crack growth response have been demonstrated which range from equilibrium cavities in rigid grains to crack-like cavities with elastic-plastic accommodation in the grains.
- Examination of the crack-tip geometry changes due to stress-enhanced chemical dissolution has identified a stress regime for stress corrosion cracking where enhanced blunting of the crack tip occurs.
- Sustained load crack growth is being characterized in an aluminum alloy (2024-T6) at 423 K. Preliminary results suggest both an incubation period prior to the onset of crack growth and a threshold stress intensity factor below which no crack growth occurs. The crack growth mechanism, as elucidated by scanning electron microscopy, was time-dependent ductile hole growth.
- To quantify the conditions required for the localization of creep damage in a material, both cavity nucleation and growth, and creep crack initiation have been investigated in the non-uniform, multiaxial stress fields that occur in the vicinity of a notch. Materials investigated include 304 stainless steel, 2½ Cr, 1 Mo steel, a reaction-bonded silicon carbide, and a sintered alpha silicon carbide.
- A facility has been constructed for fracture testing of structural ceramics at elevated temperatures to 1900 K in controlled gaseous environments such as oxygen, steam, carbon dioxide and sulfur dioxide. Initial results for silicon carbide materials indicate a sensitivity in the fracture behavior to both loading rate and environment.
- A major investigation was conducted in conjunction with the NBS Center for Building Technology to identify the prime factors in the collapse of two walkways in the Kansas City Hyatt Regency Hotel.
- An examination of the strength differential effect and the associated "plastic" volume change has been examined in two alloy systems (300 grade maraging steel and 7039 aluminum). Results indicate that the strength differential effect and the permanent volume expansion are not part of one phenomenon and do not necessarily have to occur together.

Task 12122--DURABILITY OF CERAMICS AND COMPOSITES. Our program on ceramics and composites has as its objectives: (1) the generation of new theory and data to elucidate fracture and deformation mechanisms in nonmetallic materials; (2) the development of new techniques for studying the fracture and deformation properties of materials; (3) the collection of engineering data for structural applications; (4) the investigation of processes that result in strength degradation and wear of nonmetallic materials; and (5) the investigation of the microstructure of nonmetallic materials and its relationship to mechanical behavior. Experimental techniques developed by the Division permit measurements of the mechanical properties of composites and ceramics over a wide range of conditions: in vacuum at temperatures to 2973 K, in corrosive environments at temperatures that range from room temperature to 1873 K, and in cryogenic environments at temperatures as low as 4 K. This range of experimental capabilities is unique.

- The mechanism for stress cracking of oxide ceramics was identified by showing that molecular species having strong acid-base character ( $H_2O$ ,  $NH_3$ ) are the prime contributors to subcritical crack growth of these materials.
- A new mapping procedure was developed as an alternative to the pure fracture mechanics approach to lifetime prediction. An approach such as this is required for high temperature structural applications, for which flaw nucleation often occurs.
- The durability of cements for geothermal applications was evaluated in both "down-hole" tests conducted in Mexico, and hydrothermal tests conducted at the National Bureau of Standards. A satisfactory correlation was obtained between the two types of tests, suggesting that the less expensive laboratory test can be used as a predictor of the behavior in geothermal environments.
- A dynamic hardness tester has been constructed, and is currently being used to characterize the dynamic response of ceramic and metallic materials to impulse loads. The instrument is capable of delivering loads as high as 10 Newtons in times as short as 1 ms. All materials (copper, tungsten, glass) studied to date increase in hardness as the impulse time is decreased.
- The scanning transmission electron microscope was used to demonstrate plastic deformation in  $MgO$  during controlled crack growth. Preliminary analysis of the dislocation patterns indicate that dislocations from the crack tip do not lead to significant crack tip blunting, a finding that is consistent with the "crack-tip shielding" model of crack growth.

Task 12123--ELASTIC-PLASTIC FRACTURE MECHANICS. This task addresses establishment of a science basis to develop fracture prevention requirements for structural materials which exhibit plastic fracture behavior and which are used in many commonplace engineering structures such as bridges, pipelines, ships, and pressure vessels.

- Allowable flaw-size curves and EMAT inspection system were complete for gas-line girth-welds.
- Completed fitness-for-service assessment procedures for HY130 steel for naval structures using elastic-plastic-fracture mechanics.
- Modeled influence of dislocation-shielding on crack-tip deformation.
- Developed a new test method to characterize crack arrest under elastic-plastic conditions.
- Established capability to conduct elastic-plastic finite element analyses of cracked structures.
- Validated test methodology for investigation of fatigue crack growth in regions of contained plasticity.
- Developed theory and experimental procedures for measuring residual stresses in textural plates using horizontal shear waves.



## FRACTURE MECHANISMS AND ANALYSES

### Task 12121

For structural materials, a knowledge of the fundamentals of crack-tip structures and processes is essential to understanding fracture in these materials and to predicting their long-term service life. Influences of atomic structure and chemical reactions at crack-tips have been demonstrated with atomistic models of fracture in a solid, but these influences are only beginning to be confirmed quantitatively by experimental studies of subcritical crack growth and environmental effects. Ductile processes in the high-stress region of the crack tip are being introduced into these atomistic models to assess the role of plastic deformation and to extend the theoretical models to describe crack-growth phenomena such as creep crack growth and fatigue. High-temperature fracture is a complex process with competitive fracture mechanisms, such as subcritical crack growth, cavity nucleation and growth, and grain-boundary sliding; it is affected by microstructure, impurity content and segregation, processing history, and environment.

Failure analysis studies perform a valuable service for those Government agencies that have no testing facilities and require research on the safety of structural materials. By using modern metallographic, x-ray, fractographic, and chemical analyses techniques and by maintaining a Failure Information Center, our Division serves as a focal point for analyses and compilation of many critical structural failures.

Our Division program on fracture mechanisms and failure analyses has as its objectives a broad spectrum of goals: (1) the development of fundamental theories on crack-tip structures and processes, (2) the generation of data to elucidate these crack-tip mechanisms, (3) the development of fracture methodologies for predicting structural reliability, and (4) the application of established methodologies in the analysis of actual failures. In addition, the NBS Materials Durability Program has provided funding for increased emphasis on high-temperature fracture processes and mechanisms. Our understanding of the fracture of metals under time-dependent conditions will be increased by research on crack-tip theory coupled with high-temperature tensile, creep, and fatigue properties.

#### Fracture Theory

##### Subtask 1 of Task 12121

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Predictions of crack growth and fracture and, hence, of component reliability can only be attained rationally through a fundamental understanding of crack-tip structures and crack-tip processes. In this subtask, theories are being developed to study these fracture mechanisms.

#### Lattice Theories of Fracture

The desire for understanding at a fundamental level has provided considerable impetus to atomistic modeling of cracks and crack-tip processes. In previous research on a one-dimensional lattice model of a crack, we

showed how the discrete nature of bond rupture exhibits energy barriers to brittle crack propagation and how these barriers resisting thermally activated crack propagation are related to idealized interatomic force laws for a material. A major result was the demonstration that the formalism decomposes in a manner which illustrates that the driving force for crack motion is supplied by the linear response of the entire system to the external stress (i.e., the strain energy release rate) and that the resistance to crack motion is supplied predominantly by the few nonlinear interatomic interactions at the crack tip. From this result we were able to place some bounds on the functional form for the stress dependence of the crack growth rate. By utilizing a defect Green's function approach, we have now generalized these results to two-dimensional and, to some extent, three-dimensional crack configurations. This extension allows us to consider aspects of the analysis related to more realistic crack configurations. Results indicate the importance of details of the cohesive force laws on the specific character of fracture phenomena and how chemically assisted bond rupture at the crack tip influences these phenomena.

### Stability of Sharp Cracks Against Intrinsic Ductile Blunting

Another area where atomistic modeling of crack tip processes can provide fundamental understanding is in assessing the role of ductile processes in the highly stressed region near the crack tip. A basic question in this regard is whether an atomically sharp crack is mechanically stable in a crystal; or whether it breaks down in shear by intrinsic ductility processes at the crack tip. We are not concerned here with the blunting caused by dislocations which have been created by sources external to the crack and which subsequently collide with the tip, but with the basic stability of the tip configuration of a sharp crack in a crystalline lattice. This problem was first addressed seriously by Kelly, Tyson, and Cottrell, who compared the relative magnitudes of the maximum tensile stress to the maximum shear stress in the vicinity of a sharp crack with that of the theoretical tensile strength to shear strength of the material. In a different approach, Rice and Thomson calculated the activation energy barrier for spontaneous emission of a dislocation from the crack tip. Since the stresses near a crack are highly inhomogeneous, and there is significant dispersion in the phonon spectrum of crystals, it was thought by Rice and Thomson that calculation of an actual dislocation emission event more nearly approximated the stability criterion for materials. In recent considerations of these stability criteria we have shown that the two approaches are basically equivalent in that they reflect the same kind of physics behind the stability problem. This is an interesting result due to a comparison of computer simulation studies by Tyson, which suggested that the two criteria lead to different results. Further considerations of the stability criteria have addressed fundamental issues regarding: the relationship between the activation energy for dislocation emission and the Peierls energy; the interactions between dislocations in multiple emission events with the possibility for an emission cut-off; the prospects for combined cleavage and dislocation emission; and the influence of chemical attack on the stability criteria.



## Dislocation Shielding of a Crack

When a crack is stable against spontaneous dislocation emission with its concomitant crack-tip blunting, it is still possible for ductile processes in the vicinity of the crack tip to contribute to an enhanced fracture toughness. We think here of a sharp crack embedded in a material containing external dislocation sources distributed randomly around the crack tip; but on probabilistic grounds, the tip is not likely to experience the blunting catastrophe that would occur if a slip plane intersected the exact position of the tip over a significant region of the crack front and thereby destroyed its sharp character. Rather, slip taking place ahead of the crack tip passes by without changing the geometric configuration of the cohesive zone, and slip taking place behind the crack tip cuts the cleavage surface to create a macroscopically "blunted" crack. Modeling of such fracture processes has developed by considering plasticity effects both at a quasi-continuum level and at a discrete dislocation level. In the quasi-continuum approach, a sharp crack contained in an "elastic enclave" is embedded in a continuum elastic-plastic material with the continuum plasticity, due to atomistic considerations, being required to cut-off at the elastic enclave boundary. Such models lead to calculation of increased toughness due to plasticity shielding of the stress field in the elastic enclave; but specific results appear to be model specific, depending strongly on estimates of the ratio of the plastic zone radius to the elastic enclave radius. To address these difficulties, models have been developed that consider the interaction of discrete dislocations with the crack-tip stress field. In these relatively self-consistent dislocation models, the boundary condition at the elastic enclave is not a problem. The essential features of these models are similar to the classical Bilby-Cottrell-Swinden (BCS) model of one-dimensional slip in front of a crack, but include an elastic enclave, or dislocation free zone, ahead of the crack tip.

## Grain-Boundary Chemistry and Structure

Crack tip structures and crack tip processes are strongly influenced by localized variations in chemistry. The predominant factor influencing such variations is microsegregation; in particular, segregation to grain boundaries. Although models based on thermodynamic equilibrium or vacancy-solute coupling have been proposed to account for observed segregate levels, their range of applicability has been limited. During the past year, an analysis of data from an NBS study of solute redistribution during grain growth has defined a mechanism of segregation in which grain boundary motion plays a dominant role. This analysis has given rise to development of a general theory of segregation applicable to all metallic systems and incorporating the ability to predict changing segregate levels from the solute-free boundary condition through full boundary saturation and to establish solute profiles and precipitate development. The theory predicts development of microsegregated regions in the interior of grains as well as at boundaries, consistent with the observation of both intergranular and transgranular failure modes. A unique aspect of the theory is the prediction of an athermal boundary structural change that is activated by attainment of full boundary solute saturation. The theory provides a method for a quantitative correlation between the level and species of segregate, fracture toughness,



and crack growth rate. It also offers insight into the atomistic mechanisms operating at the crack tip. Details of these results were presented at the Gordon Conference on Physical Metallurgy in July 1982.

### Plastic Yield Strip Model

A plastic yield strip model has been used to analyze a variety of fracture related situations. The model is based on a crack-tip opening displacement (CTOD) model of Dugdale, Bilby, Cottrell, and Swinden (D-BCS), as extended to finite geometries and structures by Heald, Spink, and Worthington (HSW). The essential feature that the D-BCS-HSW model provides is an expression for the crack extension force, which includes effects of both geometry and plasticity of the structure. Failure criteria are established by comparing this extension force with the crack-extension resistance. The model is described in a review of generalized failure criteria presented at the 14th National Symposium on Fracture Mechanics. The relationship between variant forms of this model, which have appeared in the literature, are discussed in this review. This paper also includes an extension of the concept of Hahn and Sarrate which says arbitrary boundaries can be established to divide fracture behavior into three categories: linear-elastic, elastic-plastic, and plastic collapse.

Using the plastic yield strip model, the fracture toughness of a pressure vessel steel was correlated with the specimen strength ratio from data reported by Server and Wullaert for several specimen configurations. This correlation has the potential of replacing costly plane-strain fracture toughness tests with simpler, and less expensive, specimen-strength-ratio measurements. A paper describing this correlation has been prepared for publication.

The model, although approximate, presents a unified picture of failure criteria and embodies many important features of the whole range of fracture mechanics from linear elastic fracture mechanics to plastic collapse. One such feature is exemplified in a residual strength diagram. This is a plot of the failure stress versus crack size for a cracked structure. In terms of this diagram, the model easily shows that for increasing fracture toughness, decreasing flow stress, or decreasing structure size, the category of linear-elastic fracture mechanics, and subsequently elastic-plastic fracture mechanics disappear. This analysis was presented at the Fifteenth National Symposium on Fracture Mechanics in College Park, MD, on July 7-9, 1982.

The model has also been applied in the ASTM "Predictive Round Robin on Fracture" sponsored by Task Group E24.06.02 on Application of Fracture Analysis Methods. It successfully predicted the failure load of 76 different specimens, consisting of three different specimen configurations (tensile, compact tension and a specially designed "three-hole" specimen), and of two different aluminum alloys with different crack sizes and width dimensions. It is also planned to apply the model to analyze pressure vessel failures as part of a study on railroad tank-car failures.

## Fracture Mechanics Concepts

A "Survey of Fracture Toughness Testing and Data with Reference to Meaning and Applications" was started in collaboration with Professor George R. Irwin of the University of Maryland. One aspect of this survey is "A Summary of Fracture Mechanics Concepts," which presents concise definitions of the basis concepts of fracture mechanics, discusses various crack propagation mechanisms, and concludes with the concept of a fracture control plan. It will be published in the Journal of Testing and Evaluation.

## Diffusive Mechanisms of High Temperature Crack Growth

Research has continued on diffusive mechanisms of cavity growth along grain interfaces at elevated temperatures. Growth is assumed to occur by matter transport from the cavity surfaces into the grain boundary under the influence of the applied stress. Gradients of the normal stress acting on the interface drive the grain boundary diffusion, whereas the stress itself is the sum of that due to the applied stress plus a residual stress due to nonuniform matter addition to the abutting grains by self-diffusion. The coupled effects of elastic deformation and atomic diffusion result in a singular integral equation for stress, which can be solved and leads to an equation correlating applied stress to the cavity-growth rate. Three regimes of response are possible: (1) for low stresses and growth rates, the cavities maintain their equilibrium shape (Hull-Rimmer cavities) and grow in effectively rigid grains; (2) for intermediate stresses and growth rates, the cavities grow into a crack-like configuration (Chuang-Rice cavities), but the grains can still be regarded as rigid; and (3) for high stresses and rapid growth rates, the cavities maintain their crack-like configuration, but now elastic-plastic accommodation in the grains must be considered.

## Crack-Growth Mechanism Maps

Often our ability to assess a material's behavior in different environments and temperature regions depends as much on the form in which we present the engineering information as on the information itself. During the past three years, a different method of expressing crack-growth data has been developed that clearly delineates mechanisms of crack growth as a function of temperature and stress-intensity factor. Contours of constant material response, namely crack-growth rate, are plotted on a diagram of the experimentally controllable parameters: temperature and stress-intensity factor. This type of representation emphasizes changes in a material's fracture mechanism as either the temperature or the stress-intensity factor change, and thereby displays the variety of ways that a crack can grow in a material. We have used these crack-growth-mechanism maps as an aid in the critical evaluation of elevated-temperature crack growth and fracture data. They provide a broad and self-consistent picture of a material's resistance to crack growth and clearly indicate regions where data either are missing or are contradictory. These maps have been prepared for a number of materials, including a nickel-base superalloy, an aluminum alloy, a hot-pressed silicon nitride, a hot-pressed silicon carbide, and a number of silicate glasses. We are now collecting crack growth data ourselves to generate additional crack



growth mechanism maps for various silicon carbide materials and for an aluminum alloy in two different tempers.

#### Stress Corrosion Induced Crack Tip Geometry Changes

Following the basic kinetic law of the well-known Charles and Hillig theory, crack-tip geometry changes due to stress-assisted chemical attack by a hostile environmental agent were investigated. In general, four regions of geometry modification were identified depending on the magnitude of the applied stress: (1) gross blunting when  $\sigma_A < \sigma_1$ ; (2) enhanced blunting near the crack tip when  $\sigma_1 < \sigma_A < \sigma_f$ ; (3) gross crack-tip sharpening when  $\sigma_f < \sigma_A < \sigma_2$ ; and (4) crack-tip sharpening with necking when  $\sigma_2 < \sigma_A$ . Evaluation of the material's parameters  $\sigma_2$  and  $\sigma_f$  for a typical material indicates Region 2 prevails in the range of stress levels which can be realistically applied. Experimental observations on stress corrosion cracking in soda-lime silicate glass support these theoretical predictions.

#### Time-Dependent Fracture Processes Subtask 2 of Task 12121

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The objectives of this subtask are to investigate time-dependent fracture mechanisms and to improve test methods for two generic categories: (1) those fracture processes that are governed by environmental effects on a material under sustained loading conditions, and (2) those fracture processes that are influenced by a strain-rate sensitivity of the material. As a counterpart of these objectives, these methods are applied to significant materials problems.

#### Hydrogen Embrittlement of Steels

Hydrogen embrittlement of important structural alloys can result in unexpected, catastrophic failure of metal components. Industrial users of these materials often must employ costly strategies to reduce the potential for embrittlement. Knowledge of bulk properties and average stress levels is often not sufficient to predict the damaging effects of hydrogen because local property differences may enhance embrittlement susceptibility. A major problem in the study of hydrogen damage has been the inability to detect and measure the local hydrogen-metal atom interactions and the effects of stress fields on this interaction. Neutron-inelastic scattering can be used to determine the effect of local stress conditions on the local atomic interaction with hydrogen. The combination of the strong interaction between dissolved hydrogen and neutrons and the deep penetration of neutrons in structural alloys offers the possibility for unique in situ measurements of the local hydrogen-lattice environment. A series of prototype experiments based on earlier results with other bcc metals have been initiated to directly



measure for the first time the local interaction of hydrogen in steel using neutron-inelastic scattering techniques.

Additional studies on hydrogen embrittlement of steels have investigated the environmental influence of hydrogen on sustained load crack growth. These studies have included: (1) a measurement technique for the permeation of hydrogen in steels; (2) a method for removal of iron sulfides from fracture surfaces that have been exposed to aqueous sulfide environments; (3) an examination of effects of temper embrittlement of steel on its susceptibility to hydrogen embrittlement; and (4) development of an automated real-time method for analyzing crack-growth rates of steels tested in aggressive aqueous environments. This year the automated method of item (4) was applied to study the behavior of a 2.25 Cr to 1.0 Mo steel tested in an acetic solution containing  $H_2S$  at 0.1 MPa (1 atm) of pressure. A publication of the results of this work describes the conditions that promote crack branching for this steel. These studies involve computed rates of crack growth from dc electrical resistance measurements of crack length in double beam (DB) type fracture-mechanics test specimens. Future studies will include measurements taken with a more sensitive ac electrical resistance system, as well as results for some thicker, compact-tension (CT) type specimens. Variables that will be included in future studies are tempering temperature for the 2.25 Cr to 1.0 Mo steel, specimen orientation with respect to rolling direction, and the partial pressure of  $H_2S$  in an aqueous acetic acid environment. In addition, work is continuing on the determination of conditions that promote the formation of branch cracks in DB specimens tested in severe sulfide environments. These studies of hydrogen embrittlement problems have been conducted under the guidance of the Subcommittee on Hydrogen Embrittlement of the Pressure Vessel Research Committee of the Welding Research Council (WRC). Work on an interpretive report to be published as a WRC Bulletin is now in progress. This work will be titled "Effects of Hydrogen on Pressure Vessel Steels." NBS personnel are actively participating in and promoting an international conference on "Current Solutions to Hydrogen Problems in Steels," which is slated for November 1982 in Washington, DC. Over 70 manuscripts have already been edited and accepted for these proceedings.

#### Creep Crack Growth

Another area of time dependent fracture response is crack growth at high temperatures. Measurement of sustained load crack growth in an aluminum alloy (2024-T6) at 423 K is in progress. The objective of this work is to develop and evaluate techniques of crack growth measurement at high temperatures, to measure the creep crack growth behavior in a few, select materials of commercial importance, and, finally, to investigate the mechanism of crack growth in these materials. To date, procedures are established for fatigue precracking and dead-weight loading fracture mechanics specimens at 423 K. From the resulting fracture surfaces, we can observe the extent of creep crack growth and deduce an approximate crack velocity versus stress intensity factor curve for this alloy. Furthermore, there is evidence of both an incubation period prior to the onset of crack growth and a threshold stress intensity factor below which no crack growth occurs. Scanning electron microscope (SEM) examination of the fracture surfaces reveals that creep crack growth was by a

mechanism resembling the fast fracture mechanism, i.e., ductile hole growth. However, the dimple density on the creep crack surface was considerably less than on the fast fracture surface. These findings explain the origins of the incubation period and the threshold stress in this material. They also shed light on the stress dependence of ductile hole nucleation at inclusions. Further experiments will be conducted on the same alloy in a harder temper (T851), and ultimately these techniques will be applied to high temperature crack growth in a heat resisting steel. Measurements will be initiated of the crack length in situ using an electric potential technique.

### Creep Fracture Processes

Another mode of failure at high temperature is characterized by a general degradation of a material's microstructure with time until fracture occurs. This process is called creep fracture. Work involves investigating the nucleation, growth, and linkage of the creep cavities that constitute the physical damage resulting in fracture under these conditions, and developing hypotheses and performing experiments which elucidate the role and interplay of these processes in the overall failure mechanism.

There are very few techniques which have sufficient resolution to study the nucleation of creep cavities. Being only nanometers in diameter, cavities at the nucleation stage of development can only be seen by high resolution transmission electron microscopy (TEM). However, it is not practical to make quantitative measurements by TEM because the number density of cavities is too small. This drawback does not apply to small-angle neutron scattering (SANS), which is sensitive to these small cavities and can probe cubic centimeters of material. For this reason, a program to measure the time evolution of the size distribution of cavities using SANS was undertaken. Preliminary SANS studies have been carried out on 304 stainless steel creep specimens.

In addition to the nucleation studies, the growth and spacial distribution of creep cavities occurring around notches in 304 stainless steel and 2-1/4 Cr to 1 Mo steel have been monitored using quantitative microscopy. Observations show the results of both nucleation and growth of cavities in nonuniform, multiaxial stress fields. This is providing the basis for quantifying the conditions required for localization of the creep damage in the region of the notch as opposed to a general degradation of the whole specimen. The findings of this research were recently presented at an international conference on defects, fracture and fatigue held in Canada and will be published in the proceedings of that conference.

Finally, notched bend bars of a ceramic material are being treated at very high temperatures to investigate the linking of the cavities to each other or to the notch to form a critical crack that results in rapid fracture. Details of this research were presented in August 1982 at the Gordon conference on Solid State Studies on Ceramics.

### High-Temperature Fracture in Reactive Environments

Materials used in the elevated temperature regions of fossil-fuel fired systems are subjected to the aggressive environments that are produced



by the fossil fuel combustion processes. These aggressive environments can adversely influence the microstructural properties of these materials, which in turn can influence the structural integrity of the material. In addition, when a component constructed from these materials is subjected to an applied stress, the environment and stress can act synergistically to degrade the structural integrity of the component. Because of the numerous structural applications for ceramics in high-temperature regions of coal conversion systems (e.g., heat exchanger and gas-fired turbine components), an understanding of the critical factors that determine the thermochemical/mechanical integrity of these ceramic materials is essential.

To address these issues, a facility has been constructed at NBS for the fracture testing of structural ceramics at elevated temperatures in controlled gaseous environments. The system consists of an enclosed electric furnace, capable of temperatures up to 1600 °C, which is installed in an universal testing machine. The gaseous test environment, except steam, is supplied to the furnace from tanks through a mass flow controller. A steam generator was constructed to generate the appropriate partial pressure of steam. The total pressure is nominally one atmosphere and the flow rate through the furnace cavity is nominally 500 mL/min. Using this facility, fracture toughness tests have been conducted on chevron-notched, four-point flexural specimens of two silicon carbide materials in an environment of nitrogen, oxygen, steam, carbon dioxide and sulfur dioxide. These experiments were conducted as a function of both temperature and rate of loading. The value of toughness measured at rapid loading rates determines the value of  $K_{IC}$  at that temperature, and the values measured at the slower rates give an indication of the extent of subcritical crack growth and/or creep blunting, yielding lower values in the former case and higher values in the latter case. Results of these fracture experiments for an alpha silicon carbide indicate very little influence of either loading rate or environment. In contrast, a siliconized silicon carbide material shows a strong sensitivity to loading rate and some sensitivity to environment. Future research with this facility will also include high-temperature crack growth measurements.

#### Critical Evaluation of Four-point Flexural Test

Crack-growth experiments are often conducted in four-point flexure. A critical evaluation of the use of four-point flexure techniques to obtain crack-growth parameters was made to determine the precision and accuracy of results obtained from these experiments. We first derived the governing nonlinear ordinary differential equations which characterize the time-history of the flexural test parameters for a given elastic brittle material exhibiting a power-law crack growth behavior. A numerical solution scheme was then developed which is capable of solving the initial value problem, thus quantitatively assessing the influence of crack growth on the load versus displacement output. The results of this analysis show that (1) higher loading rates result in higher peak loads, (2) conventional methods of evaluating  $K_{IC}$  overestimated the true value, and (3) for high N materials (where N is the exponent in the power-law crack growth equation), the flexural test method yields a broad error band in the prediction for N and hence is not a reliable



technique. However, the technique still can be used to screen quickly new materials which are potential candidates for structural applications.

### Fracture Under Impact Loading

Impact-test studies in our laboratory have centered on both the pendulum and drop-weight tests, which are used to measure the fracture toughness of metals and alloys at high strain rates. Results of these impact tests are often useful in fracture control, on the basis of either service experience or empirical correlations with fracture mechanics tests. Pendulum testing includes tests of both standard and precracked Charpy V-notch (CVN) type specimens. Test-method-development activities for CVN testing have involved our participation in ASTM activities on the development of standard test methods for precracked CVN specimens. Results of our work will appear in a publication on the significance of CVN precracking variables in determining test responses of precracked slow-bend test specimens. Drop-weight testing includes dynamic-tear (DT) tests and drop-weight NDT tests. Test-method-development activities have involved publication of a method for computer-assisted testing and data analysis for these impact tests. Future work will include results of analyses of several alternative methods for the measurement of energy absorption in DT and CVN tests. Applications in which impact testing has been used to serve Government agencies include works on plate materials used for railroad tank cars and in pipelines, as well as structural steels used in highway bridges.

### Microstructural Effects on Impact Fracture

Of considerable interest to many users of a material is the effect of small variations in the microstructure of that material on its mechanical properties. In conjunction with a NAVSEA program to develop an alternate to HY 80 steel for use in ships and submarines, we are investigating the effect of microstructural variations on the impact fracture properties of a precipitation hardened HSLA steel. Variations in grain size and precipitate distribution have been induced in this alloy by 27 different austenitizing and thermal aging treatments. We are presently characterizing the microstructure using optical metallography, scanning transmission electron microscopy, x-ray diffraction techniques, and small angle neutron scattering. Charpy impact specimens are being prepared to determine the impact properties of the various microstructures. The impact behavior will be correlated to the microstructure and the heat treatment where possible using existing theories of fracture by cleavage and ductile hole growth. In particular, we will determine the sensitivity of the impact properties of the alloy to variations in heat treatment and microstructure.

### Material Performance Center Subtask 3 of Task 12121

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The Material Performance Center assists the coal conversion industry in extending the useful life and reliability of plant components by maintaining a central source of information on the performance, especially failures,

of materials and components used in coal conversion environments. It provides an integrated material-properties data base for construction materials to aid in the design, construction, and operation of coal conversion plants. Finally, it collects and evaluates the information, maintains computer files for convenient retrieval, and disseminates the data in convenient form to users.

Sources of the information compiled by the Material Performance Center include operators of all gasification and liquefaction processes, from bench-scale units through operating pilot plants participating in the DOE voluntary failure reporting program. Information detail varies from one-page failure-occurrence reports to final reports of laboratory analyses of failed parts.

A computerized data base of approximately five hundred reported failures has been established and is continually being updated, refined, and increased as additional failure reports are received. Separate information items addressing the same failure are collated when possible. In addition, direct contact with operating personnel at the various process locations and with failure analysis laboratory staff has enhanced the quality and the flow of information and has assisted plant operators in problem solving.

At present, the Center produces sets of abstracts covering all reported incidents. The abstracts are intensive summaries constructed from the source document and they contain all reported data. They are sorted according to material, component type, failure mode, and conversion process, or any combination of these factors.

The major effort for the past year has been completion of a handbook, Construction Materials for Coal Gasification--Performance and Properties Data. This book contains data on mechanical properties and corrosion resistance gained in practical plant experience and in laboratory testing programs. It deals with the information in the context of eleven separate component areas of coal gasification plants and draws from this information an indication of possible candidate materials of construction. A separate section of the book includes tabulated data for the chemical, physical, and mechanical properties of candidate materials. The book consists of loose-leaf pages so that extending and revising the data base can be done periodically and easily.

#### Failure Avoidance Services

##### Subtask 4 of Task 12121

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Failure avoidance services provided to other Government agencies and other Divisions within NBS include diagnostic failure analysis, mechanical-properties testing, metallographic analysis, and metallurgical consultation. The results of this work have been used to assist in the development of safety regulations, in the selection of materials to improve the reliability of components and structures, and in the development of improved test methods and standards. In many cases, diagnostic failure analysis of



failed components has led to the identification of needed research in materials characterization, and this research is now part of the on-going programs described in this report. During the present year, several reports of specific projects in failure analysis and failure avoidance were completed. As in previous years, projects were completed for the National Transportation Safety Board, the Consumer Product Safety Commission, the Federal Railroad Administration, and the Office of Hazardous Materials. Special projects were completed for other Federal agencies. Reports of these investigations are shown in the list of publications in this report.

#### Failure Analyses in Transportation Systems

Contributions to a diagnostic failure investigation for the National Transportation Safety Board (NTSB) were completed on a section of failed gas pipeline. Results of this investigation are used by NTSB to identify potential hazards in transportation systems and to advise the Department of Transportation on the need for improved safety regulations.

Failure investigations were completed on failed piping and pressure vessels for the Materials Transportation Bureau (MTB) of the Department of Transportation. The results of these investigations are used by MTB to develop a data base on failure experiences in pressure vessels and piping and to determine if modifications to their safety regulation are required. A major investigation was completed to identify the cause of leaking in a large liquefied natural gas (LNG) tank. This investigation assisted the Department of Transportation in having the LNG facility repaired.

Continuing work for the Federal Railroad Administration involves identification of the causes of failure in railway tank cars and wheels. For tank cars, the work involves considerations for fracture safe design and improved materials to resist fracture in the event of tank-car accidents. The current studies involve the application of a plastic yield strip model to analyze failure criteria for through-cracked pressure vessels (for further description of this modeling effort, see the description of this model in Subtask 1). The extreme hazard resulting from frequent accidents involving tank cars containing hazardous materials is a national problem of growing significance. Results of the NBS work on tank-car materials have assisted in the development of specifications for new tank cars that will significantly reduce the frequency of major tank-car accidents. For railroad wheels, current efforts are focused on analyses of selected wheels failed in service and residual stress of wheels in service.

#### Failure Analyses in Consumer Products

Electrical receptacles thought to be possible initiation sources of residential fires were examined for the Consumer Product Safety Commission (CPSC). The results of this investigation may be used by CPSC to assess the need for modifications to the design of materials used in these products to reduce the risk of injury to the public.



## Failure Analysis of the Kansas City Hyatt-Regency Hotel Walkways

A major investigation was conducted in conjunction with the NBS Center for Building Technology to identify the prime factors in the collapse of the two Kansas City Hyatt Regency Hotel Walkways. The results of this investigation are expected to lead to a better definition of responsibility in building construction, ranging from code enforcers through detailers, as well as to a better definition of required inspection during construction. This investigation was also carried out in response to the right of the public to know how and why such a catastrophic accident occurred.

## Mechanical Failures Prevention Group

The dissemination of information to assist in Failure Avoidance was continued by the NBS sponsorship of two meetings of the Mechanical Failures Prevention Group (MFPG). These meetings were organized by the Fracture and Deformation Division. A meeting with the theme "Damage Prevention in the Transportation Environment," was held in October 1981. The April 1982 meeting addressed the theme, "Time-Dependent Failure Mechanisms and Assessment Methodologies," which generated substantial participation from both the industrial and academic sectors as well as from government laboratories. The Symposium had a strong international flavor with contributed papers from Canada, Great Britain, France, and Denmark and successfully focused on the theme of relating assessment methodologies to time-dependent failure mechanisms. A diversity of mechanisms, including dynamic machinery failure, stress-corrosion cracking, elevated temperature failure, delayed failure, and wear were discussed and illustrated for various materials, including metals and several classes of non-metals.

## Plastic Deformation of Metals Subtask 5 of Task 12121

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## Microdeformation of Metals

The commercial importance of dimensionally stable members and structures is the basis for this research. Frames and fixtures for metrology, for inertial guidance systems in both commercial and military uses, and for communication "mirrors" are all examples of commercial applications which depend on this common feature of different construction materials. The program addresses microdeformation in these materials, by studies of response to various modes of loading. An information data base is developing which will include both the microyield strength and the microcreep characteristics (for up to several thousand hours in some cases). The materials under study are aluminum, beryllium, gauge block steel, and Super Invar. The overall technical goals of this study are: (1) to develop a data base, and preferably a model, for the dependence of the deformation on very low stresses at temperatures near room temperature (with typical strains of less than  $10^{-6}$ ); (2) to characterize the interdependence between the yield and the creep modes; and (3) to develop a fundamental understanding of the dislocation processes that limit

microstrains. The program involves the combined efforts of NBS workers in Materials Science and Metrology, along with researchers at the C. S. Draper Laboratory (Cambridge, MA), Lawrence Livermore Laboratory (Livermore, CA), and Rockwell International (Huntington Beach, CA).

To study microdeformation, three different test systems have been developed at NBS. Two of these systems are for uniaxial measurements and the third system is for biaxial creep. All three systems have a basic resolution of  $10^{-8}$  strain, but have different scatter bands for long-time data. Using capacitance gauging, the two test frames for one of the uniaxial systems have scatter bands within a limit of  $10^{-7}$  strain. The other uniaxial system uses a polarizing laser interferometer and is expected to have a much narrower scatter band on the order of  $10^{-8}$ . Performance of the  $10^{-8}$  system is still being evaluated along with the initial 14,000 hours of test results from the six biaxial test frames.

Using the  $10^{-7}$  strain system for testing I-400 microcreep was found to have several notable features. Firstly, the creep strain depends linearly on the applied stress between 100 kPa and 200 MPa, and within the limited temperature range of interest (298 to 373 K), has no obvious temperature dependence. Secondly, the microcreep curve depends on the logarithm of time rather than a power of time. And lastly, the microcreep behavior is dominated by strain hardening, and after several hundred hours, an apparent "exhaustion" occurs. All three features of the microcreep behavior are consistent with Cottrell's "Exhaustion Creep Theory". In addition, a tie between the microcreep and microyield strength was found. Currently, the obstacle to the development of a firm correlation between the two deformation modes is the need for a better analytical approach for determining the microyield strength.

Statistical aspects of fitting microcreep data to creep relationships are also being developed. Confidence limits for various nonlinear curve fits have been established which allow extrapolation of the microcreep strains to times beyond the test times. This extrapolation can be done for several creep theories, including Hart's model for exhaustion creep.

Next year, the focus will be on increased consideration of test materials other than I-400 beryllium, development of a better method for determining the microyield strength, and further consideration of Hart's theory of exhaustion creep.

### Dynamic Hardness

Because of the importance of hardness to the nucleation of cracks and to other wear mechanisms during erosion, an attempt is being made to measure the dynamic hardness of metals and ceramics. This is a joint effort of Tasks 12121 and 12122. Two approaches were taken to obtain estimates of dynamic hardness. One of these approaches was directed at the characterization of acoustic signals generated during impact, so that an impact-load, time profile could be obtained for real-time impact situations. The impact apparatus has been constructed, is currently operational, and is being used for investigations of dynamic hardness of metals and ceramics. The other approach for measuring dynamic hardness uses an electrically driven hardness indenter. The apparatus--as now constructed--operates



over several decades of time,  $10^{-4}$  to  $10^{-4}$  seconds; and more importantly is capable of developing several different wave forms for the penetration load. These shapes include: (1) impulse, (2) triangle, (3) square, and (4) ramp. By using a linear current gain amplifier penetration loads up to 10 Newtons can be used to study the effect of rate on the microhardness of materials. Current emphasis for the equipment development is in devising a means of sensing the displacement of the indenter into the sample. This will be done using electrical transducers.

#### Microstructural Effects On Plastic Deformation

In conjunction with the investigation of microstructural effects on impact fracture (see Subtask 2 of Task 12121), we are also studying the effect of microstructural variables on the yield stress, the hardness, and the strain hardening and plastic instability behavior, of a precipitation hardened high strength low alloy (HSLA) steel. Here, we have induced variations in grain size and precipitate distribution in this one alloy by variations in austenitizing and aging treatments. We are presently characterizing the microstructure using optical microscopy, scanning transmission electron microscopy (STEM), and SANS. We will soon measure the plastic properties and correlate them with the microstructure when possible using elements of dislocation theory. Most importantly for users of this steel, we will determine how sensitive the deformation behavior of this steel is to variations in heat treatment and microstructure.

#### Strength Differential Effect

Most design codes assume that the yield stress in tension is the same as that in compression. Over the past year, we have been studying the microstructure and physical properties of alloys which exhibit a 5 to 10 percent difference between yield stresses in tension and in compression. Of the various hypotheses offered in the literature to explain this phenomenon, we have found that only one, based on a pressure dependent coherency strain around precipitates, applies to the alloy systems studied here (300 grade maraging steel and 7039 aluminum). We have derived analytical expressions which not only predict the existence of a strength differential, but which quantitatively give the correct magnitude in the case where data are available. These expressions are deterministic and based only on two fundamental quantities: the elastic moduli and lattice parameters.

There is often a permanent or plastic volume expansion associated with the deformation of materials exhibiting a strength differential. Since the mathematical theory of plasticity usually assumes plastic incompressibility, the above permanent volume expansion has far reaching effects when calculating the plastic deformation in such materials. We have measured such an expansion as a function of plastic strain using high resolution density determinations. The physical source of this expansion was sought using optical metallography, wide angle x-ray and neutron diffraction, scanning transmission electron microscopy, and small-angle neutron diffraction. The tentative conclusion from these investigations at present is that the strengthening precipitates are being cut up and redissolved by the dislocation motion associated with plastic deformation. Further work in the TEM and STEM is in progress. We also intend to use



differential scanning calorimetry and in situ resistivity measurements during straining to investigate further the physical source of the permanent expansion. It appears at present that the strength differential and the permanent volume expansion are not part of one phenomenon and do not necessarily have to occur together.

#### Test Methods and Standards

##### Subtask 6 of Task 12121

J. G. Early, R. J. Fields, G. E. Hicho, C. G. Interrante, J. H. Smith, and D. E. Harne, S. R. Low, and L. C. Smith

The development of test methods and standards for characterizing and specifying materials is a major activity of the Fracture and Deformation Division. The need for specific test methods and materials standards is often initially identified through our failure-avoidance efforts conducted for other Government agencies. The current activities are summarized as follows:

#### Development of Standard Reference Materials (SRM)

Under the sponsorship of the NBS Office of Standard Reference Materials, SRMs have been prepared to aid in the calibration of x-ray diffraction equipment used to determine the percentage of retained austenite in hardened steels. Austenitic stainless steel (AISI 310) and ferritic stainless steel (AISI 430) powders were blended, compacted, and sintered using powder metallurgical techniques. The samples were then calibrated using x-ray fluorescence and quantitative metallographic technique and certified for sale. During the past year, 200 - 5%, 200 - 30%, and 400 - 2.5% austenite in ferrite SRMs were offered for sale by the Office of Standard Reference Materials. The availability of this series of SRMs is essential for the accurate calibration of x-ray diffraction equipment which is used for determining the retained austenite in ferrous materials purchased according to specifications that place a maximum on the amount of retained austenite allowed. In the coming year, the possibility will be explored for the development of a SRM containing 10 percent ferrite in an austenite material. This SRM would be used to characterize the volume percent of ferrite in stainless steel welds.

#### Standard Test Methods for Hydrogen-Assisted Cracking

Hydrogen-assisted cracking (HAC) is a significant cause of unexpected fracture in structures made from ferrous alloys. Reliable test methods for assessing the susceptibility to HAC are required to reduce the costs associated with these failures through control plans that use crack-growth-rate data and threshold fracture-toughness data. A method for real-time measurements of crack-length and crack-growth rates, and hence stress-intensity and threshold fracture toughness, in double-cantilever-beam (DCB) test specimens has been developed at the NBS. This test method has broad applicability for studies of the fracture behavior of metals and alloys in environments that promote slow crack growth. This year, the application of this method has resulted in two publications: one on the solutions to the problem of crack branching in test specimens subjected

to aggressive environments; and another on a method for obtaining quantitative relationships between the aggressiveness of an aqueous environment and the susceptibility of steel to cracking. This work is conducted under the guidance of the Pressure Vessel Research Committee of the Welding Research Council.

In earlier work on the measurement of the thermal diffusivity of hydrogen in metals, an original test method was developed at the NBS using palladium specimens. This test method has applicability to the diffusivity of hydrogen in ferrous alloys, and it can be used for assessing the potency for hydrogen charging associated with various hydrogen/metal systems.

A project has been initiated to use neutron-inelastic scattering to determine the effect of local stress fields on the local atomic interaction between hydrogen and iron atoms in specimens of steel under stress. Modifications to the NBS reactor time-of-flight spectrometer have been completed. Tests carried out on nonferrous alloys by Reactor Radiation Division staff indicate that hydrogen detection in the 1 to 100 ppm range is feasible.

#### Development of Test Methods for Assuring the Safety of Pressure Vessels

Research is continuing on programs for the Office of Hazardous Materials Regulations (OHMR) to develop appropriate test methods and to provide the basis for developing standards for the safe shipment of hazardous materials in portable pressure vessels. Work has been completed on assessing the validity of various mechanical properties tests used for acceptance of homogeneous seamless steel cylinders. The results of this program will permit a fair and equitable comparison to be made between cylinders manufactured in the U.S. and those in foreign countries and will ensure the same level of safety for all classes of cylinders. A program has been initiated to assess the fracture toughness of various cylinders and to assess the need for requiring fracture toughness specifications on materials used in seamless steel vessels.

An extensive program was initiated this year to develop reliable test methods and acceptance standards for the use of composite pressure vessels in the transportation of hazardous materials. At present, attention is focused on cylinders made by overwrapping aluminum cylinders with fiberglass-reinforced plastic and Kevlar. Tests are being assessed and developed for assessing the safety of these vessels in ambient environments, high temperature environments, and in aqueous environments. The results of these tests will be used by OHMR to develop specifications for allowing wide-scale use of composite cylinders.

#### Determination of Elastic Moduli Using Sonic Techniques

The Young's and shear moduli, and Poisson's ratio were determined for a 9310 gear steel using both the pulse echo and sonic resonance techniques. Three cylinders and nine strips (three strips representing one of the three orthogonal directions in the gear) of the steel were evaluated for these elastic criteria. Pulse echo results indicated that both the Young's and shear moduli could be determined with an uncertainty of



0.5 percent. Sonic resonance results for these same moduli (using only the strips) agreed quite favorably with those obtained using the pulse echo technique.

#### Analysis of Shipbuilding Materials Standards

Under United States law, United States flag vessels must satisfy applicable United States codes and further, the materials of construction of these vessels must satisfy the material requirements specified in these codes. For vessels manufactured in foreign countries, a determination must be made as to whether materials of construction produced under foreign specifications for specific components such as piping and flanges, are equivalent in performance to materials produced under approved United States specifications. The evaluation process used by inspectors for determining the compatibility between approved domestic material specifications and foreign specifications is often not uniform.

Under sponsorship of the U.S. Coast Guard, a major study was completed which contained detailed technical comparisons between foreign material specifications, principally Deutsche Industrie-Normen (DIN) standards and Japanese Industrial Standards (JIS), and selected domestic material specifications. This comparison identified technical areas of commonality, difference, and omission that could have a significant impact on component performance. The final report identifies those foreign material specifications that are equivalent to acceptable domestic specifications, those foreign specifications that are not equivalent, and those that would be equivalent if certain additional criteria were met. The Coast Guard will use the conclusions developed in this study to reduce the current case-by-case determination of equivalence and the inherent danger of inconsistent determinations of equivalence. With the encouragement of the Coast Guard, the report will be distributed throughout the domestic and foreign standards communities. An invited talk and paper detailing the approach used in carrying out this study have been given to the Society of Naval Architects and Marine Engineers.

Currently, work is being focused on the completion of a manual describing specific technical criteria and methodologies to be used in making this type of comparison. This manual will assist Coast Guard personnel and shipyard inspectors in making new evaluations of materials acceptability.

#### Development of Standards for Resource Recovery

The development and operation of resource recovery systems has been hindered by the absence of widely accepted national standards and specifications and test methods applicable to materials recovered from municipal solid waste. There is a strong need for quantitative specifications for materials recovered from municipal solid waste. Although the value of recovered materials generally increases with purity and homogeneity, the key to the usefulness of these materials, and thus their potential for increased markets, is the ability to ensure a reproducible quality. Often it is the uncertainty over impurity content that causes potential buyers of recycled materials to demand unnecessarily higher levels of scrap quality.



Recognition of this problem led the American Society for Testing and Materials (ASTM) to create a committee to bring together representatives of many diverse interests in this new field for the purpose of developing standards. An important goal of this process of developing consensus standards was to insure significant participation of all interested parties, especially the intended users of these standards, so that a strong incentive is created to apply the standards in the market place. Working with representatives of resource recovery facilities, Federal and state agencies, and industrial consumers of ferrous scrap, the first two national consensus standards for municipal ferrous scrap have been formally adopted by ASTM. With the adoption of these standards, Subcommittee E38.02, Ferrous Metals, with NBS staff in a leadership role, has now focused their efforts on developing an adequate data base for establishing precision and accuracy limits for the ferrous scrap test methods. A round robin test program with six participants has been created to develop this data base. With the cooperation of an agency of the Ontario, Canada government, almost one hundred synthetic samples of ferrous scrap were prepared and distributed to the participating laboratories. Currently, the raw test data is being collected for analysis at NBS. Completion of the testing phase is expected by fall 1982 and the final analyses reported in the spring of 1983.

### Terminology

Our work in the area of terminology is concerned mainly with terminology for fracture testing. It includes staff participation in an international committee, ISO TC164/WG on Terminology for Mechanical Testing, as well as in several national committees, the ASTM Committee on Terminology, ASTM Subcommittee E-24.05 on Terminology for Fracture Testing, and the ASM of Committee on Definitions of Metallurgical Terms. The Chairperson and Secretary of Subcommittee E-24.05 serve in a diversified set of roles to facilitate and coordinate the development of terminology within the many task groups of the eight subcommittees of Committee E-24. This terminology includes development definitions, description of terms, recommended symbols, abbreviations, and units, as well as guidelines for use of the SI Metric Practice. Another aspect of this work is the coordination of the terminology of E-24 with that of other ASTM committees and other national and international bodies concerned with terminology for fracture testing.

This year, the Standard Terminology for Fracture Testing was substantially revised and published as E616-82 in Part 10 of the ASTM Book of Standards. It now includes a standard code for designations for test specimens. In still another effort aimed at promotion of standard terminology, one of our staff co-chaired an international symposium titled "Terminology: The Cornerstone of Global Communications Through Standards," which received good international support and will likely result in the publication of the proceedings, as an ASTM STP.



## DURABILITY OF CERAMICS AND COMPOSITES

### Task 12122

Ceramic materials are used where special properties, such as chemical resistance to corrosive environments, mechanical resistance to erosion and wear, and mechanical and chemical resistance to temperature extremes, are required. In commercial applications they are used as substrates for electronic packaging, containers for nuclear waste disposal, linings for geothermal wells, components for high-temperature gas turbines and heat exchangers, thread guides and wear surfaces for the manufacture of paper and clothing, cutting tools and cutoff wheels for the shaping and finishing operations used in the manufacture of various machines and tools, and insulating linings for reactors and furnaces in the coal-conversion and petrochemical industries. In defense applications, these materials are used as radomes, missile nose cones, turbine components in portable electric-generating facilities, electronic guidance systems and bearing surfaces in gyroscopes. Because they are brittle, ceramics are usually over-designed mechanically to avoid fracture during use. The investigation of the fracture and deformation properties of these materials is need to overcome technical difficulties associated with the brittle behavior and to permit ceramics to be used in a wider range of applications.

Composite materials are highly engineered, heterogeneous materials designed to impart unique properties not achievable with conventional materials. Composites offer the possibility of high-strength, lightweight, durable structures. In typical advanced composites, the strength-to-weight ratio is an order of magnitude larger than that in normal grades of steel. Extensive commercialization of composites will result in major energy and materials savings, increased productivity, improved product safety, and improved U.S. technological innovative capabilities. For effective industrial utilization of composites materials, better understanding of their wear-out and fracture mechanisms is needed. Test methodologies and standards must be developed, the effect of flaws and interface debonding must be assessed, and damage accumulation must be accurately inspected and evaluated.

Our program on ceramics and composites has as its objectives: (1) the generation of new theory and data to elucidate fracture and deformation mechanisms in nonmetallic materials; (2) the development of new techniques for studying the fracture and deformation properties of materials; (3) the collection of engineering data for structural applications; (4) the investigation of processes that result in strength degradation and wear of nonmetallic materials; and (5) the investigation of the microstructure of nonmetallic materials and its relationship to mechanical behavior. Experimental techniques developed by the Division permit measurements of the mechanical properties of composites and ceramics over a wide range of conditions: in vacuum at temperatures to 2973 K, in corrosive environments at temperatures that range from room temperature to 1873 K, and in cryogenic environments at temperatures as low as 4 K. This range of experimental capabilities is unique.



Fundamentals of Fracture  
Subtask 1 of Task 12122

S. W. Freiman, E. R. Fuller, Jr., S. M. Wiederhorn, B. R. Lawn, E. Case, and T.-J. Chuang

In this subtask, studies are being conducted on basic fracture and deformation processes in ceramic materials. During the past year, our work on this subtask included the development of an understanding of mechanisms of subcritical crack growth in glass. Glass was selected as a material for study because of its practical value and because it serves as a model for other brittle ceramics that are susceptible to subcritical crack growth. In addition to the work on glass, crack growth studies were conducted on crystalline materials.

Chemical Reactions at Crack Tips

Mechanisms of reaction between chemical environments and glass are being studied. During the past year, the importance of hydrogen to the crack growth rate was investigated by fracture mechanics techniques. A comparison of crack growth rates for silica and soda-lime silica glass in  $H_2O$  and in  $D_2O$  has shown a positive contribution of the hydrogen atom to the overall chemical process. Studies on soda-lime silica glass conducted in 1 N DCl and 1 N NaOD solutions suggest that the isotopic effect of  $D_2O$  on crack growth is only observed in basic environments. For the present we have no explanation of this observation. During the coming year studies in acidic and basic  $D_2O$  environments will be conducted on silica glass to determine if the isotopic effect on crack growth is similarly dependent on pH for this glass.

A chemical route to subcritical crack growth in glass was established by demonstrating that only environments with the ability to act both as electron acceptors and electron donors cause crack growth in silica glass. These studies have been extended to soda-lime silica glass and it appears that the mechanism of crack growth in this glass is identical to that in amorphous silica. No direct participation of the Na ions in the crack tip reaction was observed. Thus, the mechanism of crack growth hypothesized for silica glass appears to be equally applicable to soda-lime silica glass. We suspect that this mechanism of reaction is generally applicable to all glasses.

Our work on subcritical crack growth in brittle materials is being extended to include a variety of environments and materials (other than glass). Thus, studies have already been initiated to investigate the applicability of the electron donor-acceptor concepts (discussed above) to single crystal  $MgF_2$  and  $Al_2O_3$ . These studies are being conducted in collaboration with Dr. T. A. Michalske of Sandia National Laboratories. Results to date indicate that  $Al_2O_3$  (sapphire) is very similar to silica glass in its behavior, suggesting that oxides may undergo the same types of crack tip reactions as glasses. In contrast, crack growth in more ionic solids appear to be controlled by electrostatic interactions rather than acid-base reactions with the environment. This conclusion is based in part on isotope studies on  $MgF_2$  which suggest that protons play no role in the crack tip reaction.

A paper, "A Molecular Interpretation of Stress Corrosion in Silica," by T. A. Michalske and S. W. Freiman has been published in Nature. A more complete description of the silica studies has been submitted to the Journal of the American Ceramic Society. In addition to these, two papers, one on soda-lime silica glass, the other on  $Al_2O_3$  and  $MgF_2$ , were presented at the Annual Meeting of the American Ceramic Society.

#### Crack-Tip Geometry Changes During Crack Growth

In addition to the work on crack tip reactions, the potential effect of these reactions on crack tip geometry was studied. Following the basic kinetic law of the classical Charles and Hillig theory, the change in the crack-tip geometry due to a stress-assisted chemical attack of the environment was examined. Two extreme cases were identified. In the first case the linear term in stress (i.e., the activation volume) is assumed to disappear from the kinetic equation. In this case, the fatigue limit is found to be approximately 0.8 times Griffith stress, which is the same value as predicted by the Charles and Hillig treatment. Crack sharpening accompanied by necking is also predicted if the applied stress exceeds this fatigue limit. In the second case, the quadratic term in stress (i.e., the strain energy term) in the kinetic law is neglected leaving the activation volume term as the dominant term. For this condition stress enhanced crack tip blunting is expected for a range of applied stresses. Experimental data indicates enhanced crack tip blunting and hence suggests that case two is more appropriate for the description of stress corrosion cracking in soda-lime glass.

#### New Approaches to Fracture and Deformation Subtask 2 of Task 12122

E. R. Fuller, Jr., S. M. Wiederhorn, R. J. Fields, T.-J. Chuang,  
N. J. Tighe, E. D. Case, and G. S. White

The techniques of fracture mechanics have provided engineers with new and powerful techniques to evaluate the mechanical behavior of materials and to estimate the total allowable lifetime when a structural material is subject to mechanical forces. When the mechanism of failure is well understood, fracture mechanics techniques may be used directly to obtain a prediction of lifetime. When the mechanism of failure is not well understood, fracture mechanics in combination with probability theory is needed to develop a framework for structural design. In either case, it is important to be able to characterize the flaw size and the rate at which flaws grow in ceramic materials. A major portion of the work on this subtask during the past year was directed towards achieving this goal. The work can be divided into four projects, which are in various stages of completion: (1) Optical Nondestructive Evaluation (NDE)-Light Scattering; (2) Effect of Microcracking on Elastic Properties; (3) Crack Parameters from Strength Tests; (4) Strength Degradation Maps.

#### Optical NDE: Light Scattering

Quantitative evaluation of surface cracks and defects is an increasingly important concern in NDE. However, because of mathematical difficulties in dealing with shapes of defects, use of scattered light as a quantitative



tool is limited. This project compares theoretical and measured scattering from simple surface defects. Scattered optical radiation patterns from a v-shaped groove were compared to calculations from an exact theory (developed by D. Maystre). The theoretical calculations were based upon actual diamond stylus profile measurements of the groove cross section. The theory was found to give excellent agreement with experiment, predicting the observed number and positions of the scattering peaks. Certain discrepancies between calculated and measured scattering patterns were attributed to finite beam size and variations in groove cross section. Nevertheless, these discrepancies were minor and agreement between theory and experiment was good.

Because the exact theory is cumbersome and expensive to use (due to the need for computer calculations), it is of interest to determine the size of defects at which Fraunhofer approximations can be used. Accordingly, next year, measurements will be made on scattering from grooves with trapezoidal cross sections varying in size from the resonance domain limit to the Fraunhofer region. These measurements will be compared with both the approximate and exact calculations of scattering to yield information on the relation between the flaw geometry and the observed scattering patterns.

#### Effects of Microcracking on Elasticity

Because microcracking in the form of cavitation is an important mode of strength degradation at elevated temperatures, characterization of the effect of microcracking on bulk properties of ceramics may provide a means of monitoring the strength of these materials at elevated temperatures. With this objective in mind, investigations were conducted to establish the theoretical basis for such characterization. Four microcracking-modulus decrement theories were examined to ascertain their predictive capability. Examination of elasticity data from several microcracked ceramic oxides demonstrated similar trends for the predicted Young's modulus Poisson's ratio behavior of microcracked specimens. Experimental-elasticity data were found to be in general agreement with the predicted trends.

In another part of this investigation, we discovered that  $\text{YCrO}_3$  could be used as a model material for microcracking studies. Because this material undergoes an apparent phase transition at  $1100^\circ\text{C}$ , and because the microcracks heal at temperatures less than  $1100^\circ\text{C}$ , it is possible to control grain size and crack size independently. This control is achieved by first sintering the material at  $\sim 1750^\circ\text{C}$  to obtain the desired grain size and then microcracking and annealing the material at  $< 1100^\circ\text{C}$  to obtain the desired crack size. Thus, microcracked specimens may be produced for a range of experimental purposes, all of which have the potential of yielding a more detailed understanding of the effect of cavities or microcracks on strength.

#### High Temperature Structural Ceramics

A critical evaluation of the feasibility of obtaining crack growth parameters from four-point bend tests was made. The governing nonlinear



ordinary differential equations are derived to characterize the time-history of bend test parameters for a given elastic brittle material exhibiting power law crack growth behavior. A computer algorithm was then developed to solve the initial value problem, and thus assess the influence of crack growth on the load-displacement output. The results of this analysis indicate that for high  $N$  materials (where  $N$  is the exponent in the power law crack growth equation) the flexural test method gives a broad error band in the prediction of  $N$  and hence is not a reliable test technique. However, the technique can be used by a designer to screen new materials with high  $N$  values.

In addition to the work discussed above, the critical stress intensity factor,  $K_{IC}$ , was determined as a function of temperature for several commercial grades of silicon carbide. Chevron-notched bend bars were used for these measurements because these specimens produce sharp precracks prior to rapid fracture. The  $K_{IC}$  measurements by this technique are subject to a minimum amount of scatter, and hence, are considered to be highly reliable. Measurements of  $K_{IC}$  made at two loading rates suggest that strong loading rate sensitivity is exhibited by materials that are also creep and crack growth sensitive at the temperature of measurement. These studies will be continued into the new year on a variety of ceramic materials. The results of these studies will be incorporated into crack growth mechanism maps.

#### Cavitation Crack-Growth

Creep resistant SiC-based ceramics fail by the growth and linkage of preexisting pores. To study the kinetics of this process, notched bars were loaded in bending for times up to 150 h at 1300 and 1350 °C. These specimens were loaded at a nominal stress intensity factor of  $0.8 K_{IC}$ .

After exposure the specimens were removed from the furnace, polished, and examined using quantitative metallographic techniques. From these microscopic examinations it was apparent that the cavities grow by the diffusion of material from the cavity surface to the adjacent grain boundary. The stress distribution in a creeping bend specimen is currently being analyzed in order to test the applicability of the Chuang-Rice theory of diffusive crack growth. The details of this work will be presented this summer at the Gordon Research Conference on Solid State Studies in Ceramics.

These interrupted tests will be continued next year on various grades of commercial SiC ceramics. The results of these studies will be used to determine the regime of  $K$  and  $T$  in which diffusive crack growth is important. Results of these studies will be incorporated into crack growth mechanism maps for ceramic materials.

#### Strength Degradation Maps

Strength degradation mapping provides an alternative to the pure fracture mechanics approach for lifetime prediction. Although the approach is probabilistic in nature, concepts of fracture mechanics can be factored

into the approach. Probabilistic concepts of strength are used for the construction of strength degradation maps which relate strength, failure time, and failure probability on a single diagram. These maps provide a general picture of the failure probability on a single diagram that can be used to establish engineering loads, and temperatures that are consistent with engineering requirements. Last year, a map of this sort was obtained for magnesia-doped, hot-pressed silicon nitride (NC 132); this year a map was obtained for yttria-doped, hot-pressed silicon nitride (NCX 34). A comparison of the two maps shows that the properties of NCX 34 are far superior to those of NC 132. For a given load, the NCX 34 is capable of operating at a higher temperature ( $\sim 100^\circ\text{C}$ ) than the NC 132, without long term loss in strength. Microstructural investigations suggest that creep cavitation is not a serious problem in NCX 34, whereas it is for the NC 132. Studies are underway, to evaluate the effect of temperature and strength on the microstructure of these ceramics. During the coming year, we hope to obtain strength degradation maps on several other structural ceramics (reaction bonded  $\text{Si}_3\text{N}_4$ , reaction bonded  $\text{SiC}$ , hot-pressed  $\text{Al}_2\text{O}_3$ ). The shape of the maps will be correlated with the type of deformation and fracture occurring for each material.

#### Engineering Evaluation of Ceramics Subtask 3 of Task 12122

E. R. Fuller, Jr., N. J. Tighe, S. M. Wiederhorn, S. W. Freiman, R. S. Polvani, C. L. McDaniel, R. F. Krause, Jr., and B. R. Lawn

Extensive studies are being conducted on the strength of ceramic materials intended for use in commercial and defense applications. Materials being studied include: geothermal cements that will be used to line wells that tap hot water reservoirs deep within the earth; refractories intended for use at elevated temperatures in heat exchangers; partially stabilized zirconia linings for adiabatic diesel engines; glass intended for use in solar mirrors; lead-zirconate titanate ceramics for voltage-pulse devices; and ceramic materials for biological applications. Work on this subtask is often conducted at the specific request of other government agencies.

#### Durability of Geothermal Well Cements

The durability of various cement compositions has been evaluated following periods of exposure to flowing geothermal fluids from a well in the Cerro Prieto geothermal field in Mexico. This well was provided and operated by the Comision Federal de Electricidad, who also assisted in the placement and retrieval of the cement samples. Sixteen cements, which are potential candidates for cementing operations in geothermal wells, were selected for these durability tests. Specimens were installed both in special vessels aboveground near the wellhead and in baskets which were lowered about 700 meters into the well at a temperature of  $214^\circ\text{C}$ . Two types of specimens were used in the tests: (1) 50 mm cube specimens which were precured for one day in an autoclave at  $200^\circ\text{C}$  and 20 MPa; and (2) slurries of cement which were prepared at the wellhead, cast into sandstone cups and cured under the exposure conditions. Following periods of exposure of one day, three months, six months, and one year, the durability of specimens, were evaluated by compressive



strength and water permeability measurements. The precured cubes of many of the cements showed considerable erosion with exposure time due to geothermal fluids, especially in the vessels aboveground where the cubes were directly exposed to the flowing geothermal fluids. The compressive strength of these specimens generally decreased with time and their permeability increased. In contrast, the protected sandstone-molded cements fared better, their properties generally improving with time. This type of protected exposure is probably more representative of the conditions a cement would see as a well liner. Properties of the cements were evaluated in cooperation with the Instituto de Investigaciones Electricas, Cuernavaca, Mexico.

### Polymer Concrete for Geothermal Applications

Nonmetallic materials have a number of beneficial properties for their application in geothermal systems (e.g., greater corrosion and abrasion resistance and greater load-bearing capacity per weight of structure). Offsetting these advantages are the detrimental properties of low impact strength and fracture toughness, of time-dependent crack growth behavior and of enhanced thermal stresses. In order to design effectively with these materials and to utilize them in geothermal systems, the fracture properties have to be measured for these materials and damage mechanisms resulting from exposure to geothermal environments need to be assessed. This year a program was begun to determine these properties for a polymer concrete material which has been proposed for geothermal heat exchanger pipes and pressurized vessels. Initial measurements have been made to characterize the fracture toughness and the Charpy impact strength as a function of temperature from -20 °C up to 150 °C. Research anticipated in the coming year include pressure-rupture tests with a characterization of the failure mode and failure mechanisms.

### Refractories for Heat Exchangers

The anticipated use of ceramic heat exchangers in numbers of new energy systems necessitates the evaluation of the creep-rupture behavior of refractories at elevated temperatures. The use of refractories in regenerative heat exchangers for MHD applications, for example, requires the creep behavior of refractories to be evaluated at temperatures as high as 1600 °C. Similarly, the use of non-oxide ceramics in recuperative heat exchangers also requires the creep-rupture behavior of ceramics to be evaluated at these elevated temperatures. The objective of this study is to obtain sufficient data on potential heat exchanger materials to make an intelligent decision on materials selection for these applications.

Two types of refractories are being included in the current program, (a) fused-cast oxides and (b) hot-pressed and sintered silicon carbide. Dynamic and static loads tests are being used to evaluate the high temperature strength and long term durability of these materials. The oxide ceramics have been used traditionally for lining glass melting furnaces where their compressive strength and corrosion resistance are important properties. In attempting to use these materials for other structural purposes, it is also necessary to know the high temperature tensile strength of these materials. Five compositions of fused-cast refractories are under test: alumina-zirconia-silica, alpha and beta alumina, alpha alumina, chromia alumina, and chromia alumina spinel.



Alumina-zirconia-silica retained its strength up to 1100 °C when loaded rapidly. However when slow rates of loading were used or when static loads were applied, its strength was nearly zero at 1100 °C. The strength of this material is limited by the failure of the glassy phase. By contrast, hot-pressed silicon carbide exhibited little or no creep at temperatures up to 1400 °C. The material did however exhibit a strength loss at temperatures above ~ 1100 °C compared to the strength measured at room temperature.

### Ceramics for Diesel Engines

Recent research supported by the U.S. Army and the Department of Energy at the Cummins Corporation demonstrated the practical value of adiabatic diesel engines as a means of improving the thermal efficiency of these engines. A ten percent improvement in diesel oil consumption was registered recently by the Cummins Corporation in a standard diesel engine, which had been converted into an adiabatic engine. The conversion was achieved by coating all parts of the engine contacting hot gases with zirconium oxide. Improved efficiency (up to 50 percent) is anticipated with the use of either thicker zirconia coatings, or partially stabilized zirconia inserts in the cylinder wall liners. The Department of Energy, which is supporting this research program, has requested support from NBS to evaluate the microstructure and the mechanical properties of ceramic materials currently being used in the diesel engine program. As the evaluation of these materials is consistent with our other high temperature materials program, we have agreed to assist the Department of Energy in this task. As part of this project, we will evaluate the response of partially stabilized zirconium oxide to subcritical crack growth and to thermal cycling (in the temperature range of diesel engine operation).

### Lead Zirconate Titanate Ceramics (PZT)

Lead zirconate titanate ceramics of nominal composition 95%  $\text{PbZrO}_3$  to 5%  $\text{PbTiO}_3$  exhibit piezoelectric properties and are used in devices in which a voltage pulse is required. Premature fracture of these materials reduces the pulse length and renders the device ineffective. The reliability of the material has been noted to vary from lot to lot, depending in a complex way on processing conditions.

The objective of this study is to determine whether the fracture toughness of the material is a measure of the material's ability to survive more complex and expensive functional tests. It is also the aim of this project to determine the fundamental cause for the variation in properties from lot to lot. The effects of temperature, poling condition, and applied electrical field on fracture are also being studied. Transmission electron microscopy is being used to investigate microstructural variations in materials and to understand crack tip material interactions leading to increased toughness.

Results to date have shown that the temperature dependence of the material in the pressure depoled condition is an indicator of the quality of the lot. Good lots show a maximum toughness of pressure depoled material at room temperature, while in poor lots the maximum seems to be shifted to

~ -35 °C. It is hypothesized that these shifts are related to the ability of the material at the crack tip to undergo a stress induced phase transformation. No significant effects of electrical field, or differences in lots of material in the electrically poled condition could be discerned. Transmission electron microscopy has shown variations in chemical composition and microstructure from one lot of PZT to another. A paper was presented on this work at the Annual Meeting of the American Ceramic Society in Cincinnati, OH.

### Glass for Solar Mirrors

Various glass compositions are being considered for mirrors used in solar energy collection facilities. Since these mirrors may be subjected to harsh weather conditions, i.e., high temperatures, rain, hail etc., it is important to determine their resistance to crack growth in order to predict lifetimes and to make the best material selection.

In this project, both subcritical crack growth data using double cantilever beam specimens and dynamic fatigue data on four point flexure specimens was collected for three glass compositions. All data was taken in water at room temperature. A value of the inert strength of each glass was obtained by rapid loading in dry N<sub>2</sub> gas. The crack growth parameters obtained from the dynamic fatigue data were used to construct design diagrams for each of the glasses. A statistical analysis of the uncertainty in each of the measured crack growth parameters was used to determine uncertainties in the predicted lifetimes.

### Bioceramic Materials

Another new and interesting application of ceramic materials is in the field of medicine. Certain types of ceramic materials (aluminum oxide, glass ceramics) are useful as structural components of prosthetic devices because they are biologically inert to the body environment and are relatively strong when compared with bone. Consequently, these materials are being introduced into the body in several applications: total hip replacements, anchors for artificial teeth, and artificial knee joints. Given the tendency for ceramic materials to undergo stress-corrosion cracking due to water in the environment, there is concern over the ability of these materials to perform their function in the body environment for extended periods. Because of this concern, the Division has been conducting a study to determine the effect of microstructure on stress-corrosion cracking of aluminum oxide.

During the past year, static and dynamic fatigue data were collected on implant grade Al<sub>2</sub>O<sub>3</sub>. An analysis of these data suggests that fatigue data obtained by three-point bending may result in erroneous values of fatigue parameters. Because three-point bending produces a considerable stress gradient at the tensile surface, the flaw that causes the specimen to rupture, may not be the largest flaw in the specimen. Since the lifetime prediction equations commonly in use today all assume the largest flaw to be the source of failure, basic assumptions of the lifetime prediction equations are not valid when three point bending is used as a test method. This problem does not arise when four-point bending test methods are used to obtain static fatigue data, because the stress fields on the tensile surface of the specimen is uniform.



Extensive Monte Carlo computer calculations have shown that convergence usually does not occur for trivariant regression analyses, a technique that is often used for lifetime prediction analyses. The observation that a number of roots are normally found from the regression analysis precludes use of the technique to determine the "true" value of N. The bivariate regression technique can be used, but here errors result from uncertainties in the Weibull modulus for the material. Extensive four-point bend tests are underway using indentation procedures to provide reproducible flaws for the determination of N. A paper on the current findings was presented at the Annual Meeting of the American Ceramic Society.

In the coming year we shall obtain more accurate measurements on aluminum oxide using a controlled flaw approach (see Subtask 4). Vickers indenters will be used to introduce a well-defined fracture origin, of predetermined size, for failure. This will enable highly accurate data to be obtained. A comprehensive fatigue test program is scheduled for determining crack velocity parameters for the alumina. Inert strength data will be taken on specimens with polished surface finishes to characterize the natural flaw distribution. This approach offers the prospect of predicting lifetime characteristics of prosthetic components with unprecedented specimen economy, eliminating the need to take vast quantities of fatigue data for statistical analysis.

#### Contact Processes in Ceramics Subtask 4 of Task 12122

S. M. Wiederhorn, B. R. Lawn, B. J. Hockey, D. E. Roberts, and R. S. Polvani

Contact damage studies provide valuable information on fundamental deformation and fracture properties of materials and can be used as the basis for modelling important practical processes such as erosion, wear and the machining of ceramic materials. During the past year, our effort has been directed towards the development of a detailed understanding of the fracture and plastic deformation that occurs during contact. We currently have projects concerned with: (1) indentation damage; (2) dynamic hardness; (3) effect of sliding contact on strength. In addition to these three projects, we have completed our work on the erosion of ceramic materials at elevated temperatures.

#### Indentation Damage

It is now recognized that ceramics can be deformed irreversibly at room temperature. Moreover, this deformation plays a dominant role in the initiation and propagation of cracks that control the strength and wear behavior of ceramic materials. Recognizing this fact, a considerable effort has been made in the past few years by Dr. B. R. Lawn and his colleagues at the University of New South Wales to understand the micro-mechanics of contact damage in brittle materials. With the transfer of Dr. B. R. Lawn from the University of New South Wales to the National Bureau of Standards, this effort has also been transferred to NBS. During the past few years much progress has been made on the analysis of stress fields in elastic/plastic contact. The most important finding



from these studies is the identification of the vital role of residual stresses in the associated fracture process. These stresses have been ignored in the ceramics testing literature, as a result of which much of the published data relating to strength and erosion is in error.

One of the important applications of indentation analysis lies in the evaluation of basic fracture parameters. Indentation flaws of predetermined size can be placed in strength test pieces with great control, thereby allowing for accumulation of strength data with unprecedented experimental simplicity and specimen economy. This gives a powerful tool for measuring toughness and crack velocity parameters, without the need for statistical data manipulation. This aspect of the work is at a highly developed stage and has resulted in several publications in the last year.

A second application is the characterization of flaws. Because the location of the indentation flaw, as well as the size, can be predetermined, one can follow the flaw evolution to failure throughout the entire strength test. This is a unique feature of strength analysis. Through studies of this kind we have now established that many (probably most) of the strength-controlling "natural" flaws in ceramics respond in an analogous manner to the indentation cracks, particularly as regards the influence of residual stresses. Flaws introduced by particle impact, abrasion and machining certainly fall into this category.

#### Dynamic Hardness

Because of the importance of hardness to the nucleation of cracks during short term contact events in erosion and machining, an attempt is being made to measure the dynamic hardness of ceramic materials. The method uses an electrically driven hardness indenter and operates over several decades of time,  $10^{-4}$  to  $10^{+4}$  seconds, and delivers penetration loads between 0 and 10 Newtons. The technique is capable of developing several different wave forms for the penetration load: (1) sinusoidal, (2) triangle, (3) square, and (4) ramp. Current emphasis on equipment development is directed towards the addition of a means of sensing the displacement of the indenter as it penetrates into the sample. This will be accomplished through the use of electronic transducers.

Experimental studies during the past year have been carried out on soda-lime silica glass, copper, and tungsten using sinusoidal impulse loads. As the period of impulse decreased from  $\sim 10^4$  s to  $10^{-2}$  s the hardness of these materials was found to increase by  $\sim 10$  percent for copper and glass, and by  $\sim 20$  percent for tungsten. A short note discussing this work has been accepted for publication by the Journal of Materials Science. We have also observed that the duration of load has significant influence on the threshold for crack formation in glass. During the coming year the effect of load duration on fracture will be studied extensively.

#### Effect of Sliding Contact on Strength

This area of work for the Division is intended to enhance our understanding of contact damage in structural ceramics at elevated temperatures. The

data obtained on this project will be used for the assessment of theoretical treatments of strength degradation caused by sliding contact stresses. During the past year, equipment has been constructed to measure the adhesive and frictional forces that develop between ceramics at elevated temperatures. Tests have been conducted on glasses to determine the temperatures at which the friction is enhanced as a result of adhesion at the contact interface. Studies indicate that the coefficient of friction increases precipitously at a temperature of  $\sim 200^\circ\text{C}$  below the fictive temperature. This increase in friction requires the application of both a normal and tangential load at elevated temperatures, since tests on glass indicate that adhesion does not occur at stresses less than the fictive temperature. Microscopic examination of the contact interface indicates a pronounced effect of temperature and load on the type of fracture damage that occurs as a result of contact. Plans are currently underway to evaluate the effect of the fracture damage on strength.

#### Microstructure of Ceramics Subtask 5 of Task 12122

B. J. Hockey and N. J. Tighe

The objective of this subtask is to evaluate the effect of microstructure on the mechanical properties of ceramics. Scanning and transmission electron microscopy are the principal techniques used in this task. During the past year, work was directed at (1) uses of analytical microscopy, (2) crack tip deformation, (3) microstructural analysis of PZT.

#### Analytical Microscopy

The analytical capabilities of the scanning transmission electron microscope has been used to evaluate (a) ceramics that were deformed at high temperatures and (b) thin ceramic films that were made by electron beam evaporation. Oxide and non-oxide ceramics such as alumina-zirconia, silicon nitride, and silicon carbide were deformed during static load tests and their microstructural characteristics were identified and categorized. Surface and near surface features such as oxidation pits, grain boundaries, cavities and cracks were examined using secondary electron imaging and transmission diffraction contrast imaging. Inclusions and precipitates were imaged using back-scattered electrons and identified chemically and structurally using dispersive X-ray analysis and electron diffraction analysis. The surface microstructure was correlated with the sub-surface microstructure. This analysis was used to identify and characterize the deformation mechanisms that occur in ceramic materials at elevated temperatures.

#### Thin Films

Thin evaporated films of zirconia and magnesia are being evaluated in collaboration with Dr. Farabaugh of Division 561. Films, 250 to 750 Å, were grown on cleaved mica substrates and carbon coated for examination in the STEM. The crystallinity and composition of the films were determined as a function of thickness and deposition parameters. This type



of film will be used in reference standards for electron energy loss spectroscopy (EELS) and energy dispersive X-ray analysis (EDX) in the STEM instrument.

### Crack Tip Deformation

In this effort, transmission electron microscopy (TEM) is used to define the specific role of plastic deformation during fracture. Emphasis is placed on identifying the mechanisms of dislocation emission from cracks, and in relating the nature and distribution of dislocation to current fracture criterion models.

In MgO, TEM examination has recently confirmed the occurrence of plastic deformation during controlled crack propagation. Dislocation loops are seen to emerge not only from the vicinity of arrested crack tips, and are also found along the crack path. Preliminary analysis indicates that these dislocations do not lead to significant physical blunting of the crack tip. The results support recent "crack tip shielding" models, in which dislocation emission acts solely to reduce (or "shield") the stresses acting on a fully brittle crack. At present, a complete analysis of these crack tip dislocations and their dependence on crack orientation is being conducted. The analysis will allow a definitive interpretation of the effect of deformation on fracture.

Further work will include an effort to determine whether dislocation emission originates at the actual crack tip or from internal sources located in the vicinity of the crack tip. Similar TEM studies will be made on silicon, and will include the effect of temperature.

### Microstructural Analysis of PZT

Two commercial forms of lead-zirconia titanate were examined using the CMS Philips 400 TEM/STEM analytical electron microscope. While similar in composition ( $\text{PbZrO}_3$  to 5%  $\text{PbTiO}_3$ ), the two forms were processed differently and were found to possess different mechanical properties, i.e., strength and fracture toughness.

Examination showed that both polycrystalline materials were reasonably similar with regard to: grain size, shape, and distribution; porosity; defect and domain structure; and minor impurity content. Consistent with phase diagram data, the major phases were ferroelectric with rhombohedral structures (several variants were identified).

A significant difference between the two forms, however, was found in the nature and distribution of grain-boundary phases. In the tougher, higher strength material, grain-boundary phases were inhomogeneously distributed (generally, being located near large voids or inclusions). In this material, the grain boundary phases were invariably crystalline and contained both Al and Si as major impurities. Conversely, the lower strength material contained a more uniform distribution of grain boundary phases, which were typically low density (porous) amorphous structures. While these amorphous structures were not identified, they generally contained either Al and Si or Si alone as major impurities.



While the results clearly indicate a relationship between mechanical properties and grain-boundary structure, which in turn can be related to processing technique, little information was provided on the actual processing treatments used in producing the two PZT materials.

Engineering Evaluation of Composites  
Subtask 6 of Task 12122

M. B. Kasen, R. E. Schramm, R. D. Kriz, H. M. Ledbetter, and C. M. Fortunko

Nonmetallics Property Determination and Modeling

Elastic properties, such as Young's modulus and the related property, internal friction, are fundamental to characterizing and understanding filamentary-reinforced composite materials. Several theoretical and experimental studies are in progress: (1) relationships between microscopic (constituent) properties and macroscopic (composite) properties in a cooperative program with the University of Colorado using theories based on scattered plane waves that predict sound velocities and elastic constants; these theories will be extended to ultrasonic attenuation, having been tested successfully for boron-aluminum and graphite-epoxy; (2) detection of mechanically induced damage; experiments show that the Young's modulus in graphite-epoxy can either decrease or increase depending on the deformation mechanism while internal friction always changes oppositely; (3) relationship between static and dynamic elastic constants using theory and experiment to clarify this frequently confusing correspondence; (4) internal friction of interfaces, just beginning, will probe the interrelationship among three sources of internal friction--filler, matrix, and interface; and (5) stress-induced interface strains in crossply laminae where misaligned anisotropic connected layers have strongly anisotropic interfacial strains that have been calculated from the full set of elastic constants.

We now focus on two particular problems:

(1) Ultrasonic determination of complete nine-component (orthotropic) elastic-constant tensor for a glass-fiber-cloth-reinforced composite. Equipment for room-temperature elastic-constant measurements of Young's and torsional moduli is in place and operating. Calibrations are in progress. This equipment consists of a Marx three-component oscillator where two components are identical quartz piezoelectric crystals. The specimen is the third component. This equipment operates at near-zero stress amplitude in the kHz region. Therefore, one obtains the high-frequency, adiabatic, elastic constants.

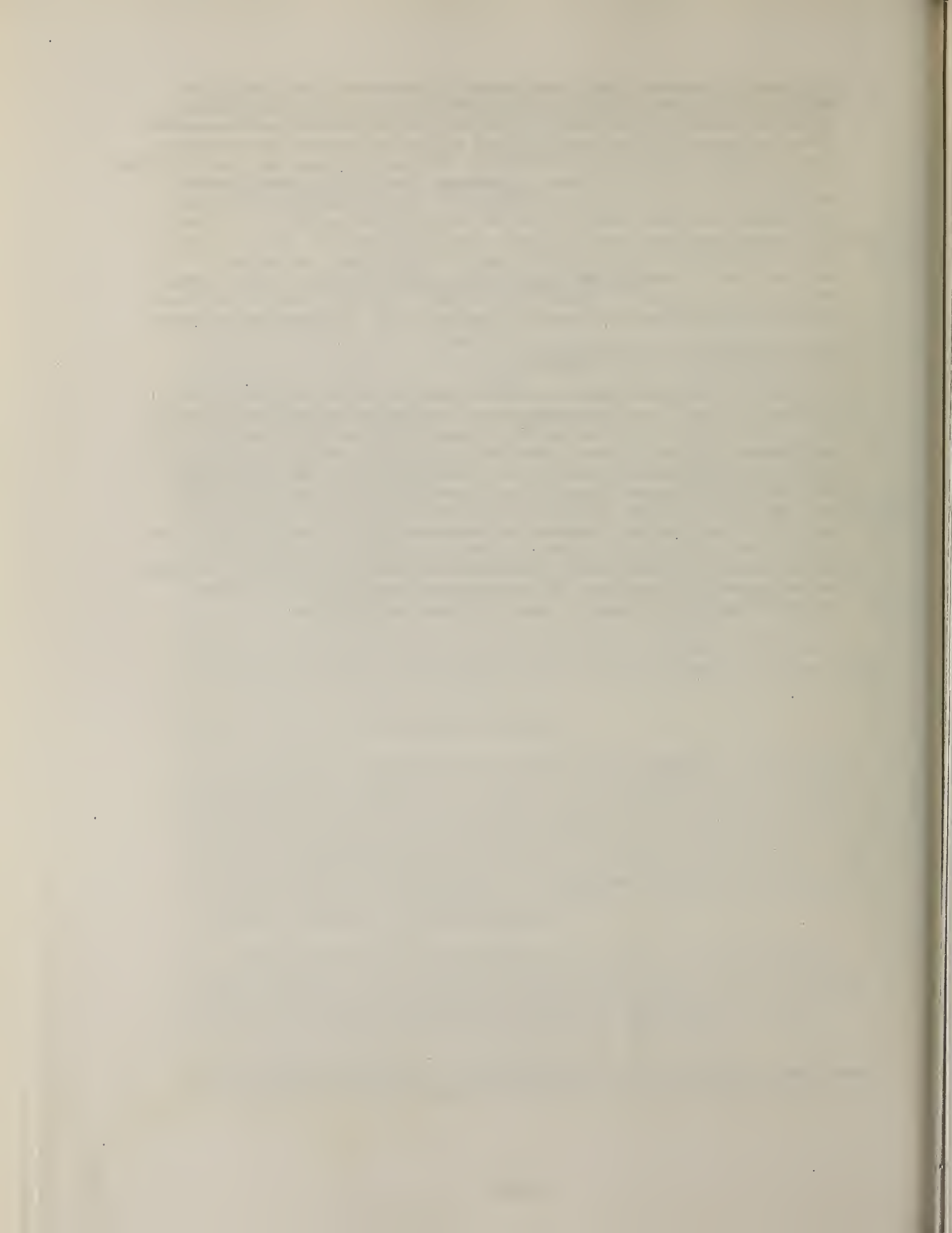
(2) Local stress in a woven-composite unit cell. A finite-element program used to predict regions of high stress within a unit structural cell is available. Element library includes constant-strain triangles modeled for nonzero out-of-plane strain with isoparametric nonzero out-of-plane element with orthotropic elastic properties.

Thermal properties, such as conductivity, are of fundamental importance in designing efficient thermal standoffs transitioning from 295 K to 4 K

in cryogenic systems. Very low conductivities make it difficult to obtain accurate measurements, and in the past, results from different laboratories were at variance. A series of studies was therefore undertaken to determine the extent to which variables such as resin content, strain effects, and specimen thickness affected the measured conductivities of G-10CR glass-reinforced epoxy laminates from various manufacturers, G-11CR, and a European laminate similar to G-10. Specimen strain at room temperature was found to have an insignificant effect, thickness differences produced detectable but negligible conductivity variations, while variations in resin content had a large effect. An equation derived from a conductivity model in which the glass and resin thermal resistances are added in proportion to their volume fractions was found to predict conductivities in good agreement with the experimental data.

#### Radiation Effects on Nonmetallics

Insulators for superconducting magnets used in fusion technology must continue to function after exposure to neutron and gamma irradiation at 4 K. Thus far, G-10CR and G-11CR laminates have been screened for such performance by ORNL, as has a variant of G-10CR in which the epoxy matrix was replaced by a polyimide. NBS provided the basic cryogenic mechanical performance data in the unirradiated state for each of the test materials. It is expected that research to develop functional, cost effective laminate systems for this service will accelerate in the coming year, with close cooperation between national laboratories, universities, and laminating firms beginning work in the area. The wish to cooperate in this effort has also been expressed by individuals representing laboratories in Japan, England, and Germany.





## ELASTIC-PLASTIC FRACTURE MECHANICS

### Task 12123

Safety and durability are primary considerations in the design and construction of engineering structures. Sophisticated methods to assess structural safety and durability have been developed on the basis of linear-elastic fracture mechanics. These analytical methods are applicable to the high-strength alloys used for aerospace vehicles and to the heavy-section steels used for nuclear pressure vessels. Unfortunately, the methods of linear-elastic fracture mechanics do not apply to a wide range of metal structures, including bridges, pressure vessels, ships, offshore structures, and pipelines, because in these applications, the materials of construction (steels and aluminum alloys are typical) are highly plastic (nonlinear) before fracture. Consequently, the assessments of structural safety and durability are based on empirical methods and prior experience. Although current methods usually provide a reasonable record of structural safety, improved efficiency and productivity could be achieved if more rational methods were used to establish material-toughness requirements, allowable stress levels, minimum service temperatures, and weld-quality standards. The objective of this task is to establish the scientific basis (i.e., elastic-plastic fracture mechanics) for developing fracture-prevention procedures applicable to materials that exhibit extensive plasticity.

### Fracture Mechanics Relationships

D. T. Read, H. I. McHenry, R. B. King, and Y.-W. Cheng

The application of elastic-plastic fracture mechanics to the assessment of structural safety hinges on the development of analytical relationships among applied strain, required toughness, and flaw size. The approach used to establish such a relationship for the elastic-plastic case is to measure the driving force for fracture as a function of strain in tensile panels with a given flaw size and configuration. The driving force for fracture is measured in terms of the J-contour integral (J) or the crack tip opening displacement (CTOD). If one assumes that fracture occurs when a critical value of J or CTOD is reached, then the measured driving force is the same as the required toughness. Thus, each test results in an empirical relationship among applied strain, flaw size, and required toughness that is directly applicable to the specimen configuration. Tests are being conducted on a variety of specimen flaw configurations to provide a data base to evaluate critically the theoretical models and finite element analysis methods of relating applied strain, required toughness, and flaw size.

Procedures for the direct measurement of J are based on the definition of the J-integral:

$$J = \int_{\Gamma} W \, dy - \vec{T} \cdot \frac{\partial \vec{u}}{\partial x} \, ds \quad (1)$$

where W is the strain energy density,  $\vec{T}$  is the traction vector,  $\vec{u}$  is the displacement vector, x and y are Cartesian position coordinates, and s is arc length along the contour,  $\Gamma$ . A convenient contour for evaluating J follows free surfaces along the y direction and traverses the tensile

axis at a location remote from the crack. Measurement of the J-integral along this contour requires determination of the strain energy density along the y-direction contour segments and measurement of traction and displacement vectors along the x-direction segments. The strain-energy density is obtained using strains measured along the contour and the stress-strain curve of an uncracked tensile panel. The y-components of the traction and displacement vectors along the x-direction contour segments are measured using strain gauges and LVDTs, respectively. The change in displacement with position,  $du/dx$ , is calculated from the measured displacements. During a typical test, approximately one hundred J-vs- $\epsilon$  data points are obtained. Each point is computed from about twenty-five measured values of strain, displacement, and load.

The J-contour integral has been measured as a function of strain,  $\epsilon$ , for HY 130 steel plates using several specimen configurations. The results indicate that the functional form of the dependence of J on strain is usually parabolic, then linear. The parabolic region at low strains is the region of linear-elastic fracture mechanics. The slopes of the linear parts of the J-vs- $\epsilon$  curves depend on crack length. As the crack length decreases to low values, deformation changes from net section yielding to gross section yielding, and the slope of the J-vs- $\epsilon$  plot decreases sharply. A design curve has been developed to relate required toughness, flaw size, and strain for the case of gross section yielding.

Finite element analyses have been conducted to calculate J-vs- $\epsilon$  for comparison with the experimental results on HY 130 plates. Analyses that assumed plane stress overestimated the measured values of crack mouth opening displacement (CMOD) and J; yet excellent agreement was observed with the experimental load-displacement and limit-load results. The discrepancy was attributed to through-thickness constraint. Three-dimensional modeling of the crack tip region is being developed to account for constraint effects.

The demonstrated usefulness of the J-integral as a measure of the driving force for fracture and as a fracture criterion for two-dimensional configurations makes it desirable to apply J in a similar fashion to three-dimensional configurations such as surface flaws. Recent research at NBS has demonstrated that the J-integral for line contours about part-through cracks is path independent for two special planes. These planes are the planes of symmetry for part-through cracks and include the plane of maximum depth of a semielliptical surface flaw. Thus, the point of maximum J along the front of a surface flaw can be evaluated using the line J-contour integral.

Given that J is path independent for the plane of symmetry of a surface flaw, it is possible to measure J-vs- $\epsilon$  using the procedures described previously. For a surface flaw centered with respect to width and length in a tensile panel, the measurement contour is in the center-width plane and extends from the crack plane up the front face of the specimen, through the thickness, and down the back face of the specimen to the crack plane. A series of surface-flawed tensile panels of API 5LX-70 pipeline steel weldments were instrumented and tested to measure J and crack opening displacement (COD) vs  $\epsilon$ .



The experimental results of  $J$  (and COD) vs  $\epsilon$  were compared with analytical results obtained using the line-spring model. In this model, the surface flaw is treated as equivalent to a through-thickness flaw of the same length that is subject to closure forces and moments due to the presence of the uncracked ligament. The closure forces are computed by balancing the forces and moments such that the COD of the through-thickness crack is compatible with the COD of an edge-cracked panel with the same thickness and crack depth as the surface-flawed panel. The ligament is treated as an elastic, perfectly plastic spring, and thus, the magnitude of the closure forces and moments remains constant after ligament yielding. The elastic, perfectly plastic spring and the constant-depth crack assumptions result in considerable simplification of the analysis, thereby avoiding the necessity of computerized numerical methods. The excellent agreement between the experimental and analytical results from both COD and  $J$  suggests that the simplifying assumptions are reasonable and that a useful and convenient method for surface-flaw calculations is available.

### Fracture Toughness

H. I. McHenry, I.-H. Lin, J. G. Early, Jr., and R. B. King

In elastic-plastic fracture mechanics, fracture toughness is generally measured in terms of  $J$  or CTOD. As currently measured, fracture toughness is not a geometry-independent material property for steels in the transition region between linear-elastic and fully ductile fracture. The critical values of  $J$  or CTOD depend on the three-dimensional stress-strain behavior in the vicinity of the crack tip, i.e., on the crack tip region constraint (CTRC). Available information indicates that CTRC is a function of geometry, type of loading, and strain hardening. Thus, a predictive fracture criterion for the elastic-plastic case should be proportional to a material property, such as the plane strain fracture toughness,  $K_{Ic}$ , and should be scaled by a function of CTRC.

A study of fracture-characterizing parameters addresses the influence of CTRC on observed fracture behavior. Especially large errors can be introduced by present measurements of critical  $J$ -integral or CTOD values for the onset of cleavage fracture; large measurement variations are due to differences in CTRC between laboratory test specimens and cracks in structures. For example, the critical values of  $J$  or CTOD obtained in deeply notched single edge-notched bend (SENB) specimens may grossly underestimate the toughness associated with identical material at the tips of smaller SENB specimens or at shallow surface cracks in large structures. Although published research indicates a growing awareness of these situations, there appears to be no generally acceptable method available at this time to determine the magnitude of the CTRC. The approach being taken is to obtain a comprehensive set of elastic-plastic fracture data (both  $J$  and CTOD) on a C-Mn steel for specimen designs having a wide range of plastic constraint. These data demonstrate geometry dependence and establish an empirical basis for developing a parameter to characterize the influence of plastic constraint.

A theoretical study of cleavage fracture is being conducted to complement the empirical studies. A model is being developed that is an extension



of the work of Ritchie, Rice, and Knott. It uses the strain-field solutions of Hutchinson to predict stress-state effects on the brittle-to-ductile fracture-mode transition. The experimental data will be used to evaluate the resulting theoretical predictions. In addition to plastic constraint effects, metallurgical factors are being investigated, particularly grain-size effects.

As part of a program to formulate guidelines and procedures for the inspection of pipeline girth welds, a fracture mechanics approach has been chosen to evaluate and assess allowable girth weld flaw sizes. The fracture toughness of the weld metal and associated HAZ are needed parameters in the criteria for accepting or rejecting a weld flaw. Crack-opening displacement (COD) tests were carried out on both weld metal and the HAZ from API 5LX-70 linepipe girth welds over the temperature range of  $-150^{\circ}\text{F}$  to  $+75^{\circ}\text{F}$  to establish the temperature dependence of the crack tip opening displacement (CTOD) toughness parameter. Using the fracture toughness temperature dependence data, a multiple specimen resistance curve approach was used to determine the critical crack tip opening displacement for the initiation of stable crack growth at the lowest temperature at which reproducible slow stable crack growth occurred. Some preliminary data were taken on the effect of specimen pretreatment to control fatigue crack shape on the measured fracture toughness.

A program to develop materials selection criteria for crack arrester strakes has been initiated. The objectives of the program are to develop experimental methods sufficient to thoroughly characterize the crack arrest event under conditions where extensive plastic deformation contributes to arrest, and to develop crack arrest criteria for the case of a crack that initiates in a low toughness plate and propagates through a weld into a crack arrester plate. Initial tests have been conducted to develop the necessary instrumentation.

A program has been started to assess the significance of fatigue cracks detected in offshore structures during in-service inspections. The objectives of the program are to investigate the fatigue crack growth behavior of surface cracks in steel weldments under simulated service conditions, to analytically model the growth of surface cracks under variable amplitude loading, and to compare the analytical predictions with the experimental results. Fulfillment of these objectives should provide the technological basis for deciding what remedial actions should be taken in the event that a fatigue crack is discovered during in-service inspection of offshore structures.

#### Significance of Defects

H. I. McHenry, M. B. Kasen, and Y.-W. Cheng

A program has been completed establishing preliminary weld-quality requirements for the Alaska Natural Gas Transportation System (ANGTS). Analytical studies involved modeling of the significance of defects using methods comparable to those used for the trans-Alaska pipeline assessment conducted previously. Experimental studies involved the measurement of CMOD as a function of remote strain for tensile panels with surface flaws. The results of these experimental and analytical

studies validate the critical COD models used in the trans-Alaska oil pipeline. These models have been used to establish the allowable flaw size curves and their sensitivities to applied stress, and material tensile flow properties were compared and evaluated.

The extent to which the through-wall dimension of typical weld flaws, such as porosity and slag, is limited by the depth of a weld pass was studied in pipeline girth welds. Confirmation of such an inherent limitation simplifies the application of fracture mechanics principles to welds inspected by conventional radiography. Both multiaxis radiography and serial sectioning were used in this work.

The probability of fracture initiating from blunt pipeline girth weld flaws was assessed in a program that subjects weldments containing slag, porosity, and arc strikes to low-cycle, strain-controlled, fully reversed fatigue within the plastic range. Results indicate that such flaws have a very low probability of initiating failure in weld metal of the toughness used in pipeline construction. The results are supportive of the concept that the allowable content of such flaws is more properly established on the basis of the percentage obscuration of a radiographic film than on flaw dimensioning.

#### Ultrasonic and Electromagnetic Techniques for Nondestructive Evaluation and Characterization

C. M. Fortunko, M. Linzer, S. J. Norton, A. H. Kahn, and R. E. Schramm

During FY 1982 significant advances were made in four areas: (1) non-contact evaluation of butt weldments; (2) noncontact measurement of in-plane residual stresses in plates; (3) eddy current characterization of sharp surface flaws; and (4) theoretical development of ultrasonic imaging techniques. In areas (1) and (2) use was made of special ultrasonic probing signals that can only be generated and detected using electromagnetic-acoustic transducers (EMATs). The special ultrasonic signals are shear waves polarized parallel to the surface of a plate (shear horizontal or SH waves). In area (3) a new high-frequency eddy current probe was developed to permit measurements of surface flaw responses over a two-decade frequency range (100 kHz to 20 MHz).

In the area of ultrasonic imaging, significant progress has been made in the areas of theoretical development of new ultrasonic techniques for characterization of material properties and detection of flaws in weldments. A new program was also initiated in the area of acoustic emission (AE) technique development using laser generation and detection.

In the area of weld inspection, three separate projects were carried out: (1) definition of inherent flaw sizing accuracy limitations for inspection of pipeline girth welds; (2) development of improved techniques for in-service monitoring of intergranular stress corrosion cracking in nuclear power plants; and (3) definition of a special noncontact SH-wave-EMAT inspection system for the U.S. Navy. The work in the area of weld inspection was carried out in collaboration with Professor S. K. Datta of the University of Colorado in Boulder, Dr. R. K. Elseley of the Rockwell International Science Center, Dr. B. W. Maxfield of the Lawrence



Livermore National Laboratory, and Mr. Marvin Fleming, a subcontractor to the Electric Power Research Institute. In addition, close relationships were maintained with other centers of research (Battelle-Northwest Laboratories, Iowa State University, and Johns Hopkins University) in the area of nondestructive evaluation of welds. Several industrial liaisons were also maintained.

In the area of ultrasonic residual stress measurement, a significant advance was made by demonstrating that the in-plane residual stresses can be determined ultrasonically in elastically anisotropic and inhomogeneous engineering alloys. Specifically, it was shown that the influences of stress and material property variations on the ultrasonic velocities can be separated. To accomplish this, a new theory was developed to relate the velocities of obliquely propagating SH-waves to in-plane stresses and weak anisotropies caused by microstructural effects. The efficacy of the technique was then demonstrated using a specially designed SH-wave-EMAT system. This work was carried out in very close collaboration with Dr. R. B. King, also of the Fracture and Deformation Division.

In the area of eddy current characterization of surface flaws, a large number of experimental measurements were carried out in support of the theoretical work carried out by Professor B. A. Auld at Stanford University. A considerable in-house theoretical effort was also conducted. As a part of the experimental effort, a novel eddy current probe design was developed, and a large number of calibrated experimental samples were prepared. As a consequence, it was possible to verify that the phases of eddy current flaw responses carry important information about the flaw depth and shape when the effects of nonuniform probe fields and electromagnetic interferences are taken into account. It is hoped that future extensions of the present work will lead to significant advances in probe design and calibration, and will help to open-up the field of eddy current imaging.

In the area of ultrasonic imaging (4), the work during FY 1982 emphasized the theoretical development of new ultrasonic imaging techniques. A perturbation method for correcting for ray refraction in velocity and attenuation tomography has been devised. This work will allow the practical generation of more accurate images of ultrasonic parameters and hence better characterization of materials properties. An imaging system based on an annular aperture has also been developed. The approach provides a reflectivity image with resolving power equivalent to that of a full circular aperture twice the diameter of the annulus. This, in turn, permits more economical and rapid imaging over a smaller area of a material surface.

New programs were initiated in the areas of technique development to (1) improve the accuracy and sensitivity of acoustic emission (AE) measurements, and (2) develop a laser-based ultrasonic remote sensing technique. In addition, work was begun on a computer-based, low-frequency ultrasonic imaging system using SH-wave electromagnetic-acoustic transducers as array elements. This work is a part of a multi-year program in cooperation with the Defense Advanced Research Projects Agency and the U.S. Navy.



## Low-Temperature Properties

R. P. Reed, R. L. Tobler, H. I. McHenry, J. M. Arvidson, and N. J. Simon

A major developing technology is the use of superconducting magnets in energy applications. High magnetic fields are required for fusion-plasma and MHD-plasma confinement and guidance. Superconducting machinery, under prototype development, provides the potential for better performance coupled with lighter weight and reduced space requirements. Energy storage, using large superconducting rings, is being considered. In all applications, the magnet or superconductor, with appropriate structural supports, is expected to operate at liquid-helium temperature (4 K) up to 30 years.

Such emphasis on liquid-helium design and material use has led to large national materials programs sponsored by DARPA and DOE and managed by this NBS Division. These programs have produced a low-temperature materials handbook; mechanical, thermal, electrical, and magnetic characterization of economical structural alloys including austenitic stainless steels, aluminum alloys, and superalloys; an annual Low-Temperature Materials Workshop held each October in Vail, CO; and joint research programs with subcontractors, which have included Battelle, Westinghouse, General Electric, Martin-Marietta, Teledyne-McKay, Alcoa, Armco, ESCO, and Japanese steel companies. Major research emphasis has been to characterize the austenitic stainless steels (AISI 304, 316, and 310 grades), to develop reliable welding processes and filler metals for welding steels, and to develop stronger, tougher austenitic stainless steels for use at low temperatures.

We are developing and characterizing a new class of austenitic stainless steels. Interstitial strengthening of a conventional austenitic Fe-Cr-Ni alloy is achieved by adding nitrogen, and increased alloy formability and nitrogen solubility limits are achieved by adding manganese. We are studying the influence of nitrogen and manganese on the temperature dependence of the flow strength, activation energies and volume, martensitic transformations, fracture toughness, and fatigue-crack-growth rates from room temperature to 4 K. Results indicate that the dependence of flow strength on nitrogen concentration increases dramatically at low temperatures. Nitrogen additions suppress martensitic transformations. A linear relationship between fracture toughness (from J-integral measurements) and tensile yield strength at 4 K has been identified. The temperature dependence of the flow strength is critically dependent on austenite stability; low austenite stability results in strain-induced martensite formation, which produces low flow strength. The anomalous stress-strain behavior resulting from martensite transformation has been analyzed and reported.

The role of low ferrite and small grain size in improving low temperature weldment fracture toughness is being studied. Crack propagation studies at 4 K through duplex ferrite-austenite cast structures has identified the application of an Ashby composite model for prediction of fracture properties.

## Elastic Deformation Phenomena

H. M. Ledbetter and M. W. Austin

Our effort on solid-state elastic constants comprises three categories: (1) measurements; (2) analysis, correlations, theory; and (3) theory-observation.

Our measurement studies deal with metals and alloys, composites (both fiber and particle reinforced), resins, and polymers. Many of these materials we study versus temperature down to four kelvins. Ongoing studies include: (1) beryllium; (2) NbTi/Cu superconductive wire; (3) SiC-reinforced aluminum; (4) Mn-alloyed stainless steels; (5) carbon-carbon composite; (6) stainless-steel welds (including some containing delta ferrite); (7) delta-ferrite castings; (8) particle-reinforced aluminum; (9) glass-fiber-epoxy; (10) graphite-epoxy; (11) polymethyl methacrylate; (12) epoxy resins; and (13) several polymers.

Analytical-correlational-theoretical studies in progress include: (1) error propagation during elastic-constant matrix inversion, for both cubic symmetry and hexagonal symmetry; (2) calculations of Debye characteristic temperatures from single-crystal elastic constants; (3) graphical representations of various elastic-constant surfaces; (4) prediction of single-crystal elastic constants for stainless steels from polycrystalline elastic constants; (5) prediction of upper and lower elastic-constant bounds of textured aggregates and application to stainless-steel welds; (6) modeling of periodically laminated composites; (7) modeling of an inhomogeneous NbTi/Cu composite superconductive wire; calculations of elastic-wave surfaces for anisotropic, especially orthorhombic-symmetry media.

In-progress theory-observation studies include: (1) in collaboration with S. K. Datta, a scattered-plane-wave theory for predicting macroscopic elastic constants of fiber-reinforced composites, including the anisotropic-fiber case, and application to boron-aluminum and graphite-epoxy; (2) in collaboration with S. K. Datta, a theory for predicting elastic constants of a ring-layered composite and application to NbTi/Cu superconductive wire; and (3) in collaboration with S. K. Datta, theories are being developed for predicting properties of particle-reinforced composites. This latter theory, based on plane-wave scattering will be quite powerful. It will include eight variables: particle properties, matrix properties, overall particle volume fraction, volume fraction of matrix "islands," particle shape, "island" shape, particle size, "island" size.

Other Activities of the  
Fracture and Deformation Division

Invited Talks

Preliminary Evaluation of LNG Storage Tank at Salem, Massachusetts  
Expert Testimony presented at Department of Transportation Hearing  
Cambridge, MA

J. H. Smith  
July 1, 1981

Effect of Deformation on the Fracture of  $\text{Si}_3\text{N}_4$  and Sialon  
2nd NATO Advanced Study Institute on Nitrogen Ceramics, Sussex  
University, Falmer, England

R. J. Fields, T.-J. Chuang and E. R. Fuller, Jr.  
July 27-August 7, 1981

Lattice Theory of Fracture  
18th Annual Meeting, Society of Engineering Science, Inc., Brown  
University, Providence, RI

R. M. Thomson and E. R. Fuller, Jr.  
September 1981

Atomistic Aspects of Brittle Fracture  
Ceramic Engineering Seminar, New York State College of Ceramics at  
Alfred University, Alfred, NY

E. R. Fuller, Jr.  
October 1, 1981

Stainless Steel Weld Inspection  
NBS-DOE Workshop, Vail, CO

C. M. Fortunko  
October 6, 1981

Fitness-for-Service  
NBS-DOE Workshop, Vail, CO

D. T. Read  
October 6, 1981

Review of Low Temperature Structural Alloy Research  
NBS-DOE Workshop, Vail, CO

R. P. Reed  
October 7, 1981

Stainless Steel Properties  
NBS-DOE Workshop, Vail, CO

R. L. Tobler  
October 7, 1981



Dynamic and Static Young's Moduli of Fiber-Reinforced Composites  
NBS-DOE Workshop, Vail, CO  
H. M. Ledbetter  
October 7, 1981

Applied J-Integral Values in Tensile Panels  
Second International Symposium on Elastic-Plastic Fracture Mechanics,  
Philadelphia, PA  
D. T. Read  
October 7, 1981

Structural Material Low Temperature Mechanical Properties  
NBS-DOE Workshop, Vail, CO  
R. P. Reed  
October 8, 1982

Mechanical Properties of CF8M Stainless Steel Castings at 4 K  
NBS-DOE Workshop, Vail, CO  
T. A. Whipple  
October 8, 1981

Handbook of Structural Materials for Superconducting Magnets  
NBS-DOE Workshop, Vail, CO  
N. J. Simon  
October 8, 1981

J Integral Analysis of Surface Flaws in Pipeline Steel Plates  
Second International Symposium on Elastic-Plastic Fracture Mechanics,  
Philadelphia, PA  
R. B. King  
October 8, 1981

Application of Fracture Mechanics to a Regulatory Problem  
ASME-ASNT Symposium on NDE Reliability, Atlanta, GA  
J. H. Smith  
October 12, 1982

Subcritical Crack Growth Mechanisms in Ceramics  
American Ceramic Society, Basic Science Division, Louisville, KY  
S. M. Wiederhorn  
October 12, 1981

Fracture Criteria for Sharp Cracks  
Fall Meeting of The Metallurgical Society of AIME and Materials  
Science Division of American Society Metals, Louisville, KY  
R. M. Thomson and E. R. Fuller, Jr.  
October 12-15, 1981

A Long Wavelength Ultrasonic Technique for Detecting and Sizing  
Weld Defects  
American Society for Nondestructive Testing, Atlanta, GA  
R. E. Schramm  
October 13, 1981

Sizing of Surface Cracks Using SH Waves  
1981 Ultrasonics Symposium, Chicago, IL  
C. M. Fortunko  
October 14, 1981

Improvements in Flaw Detection and Sizing in Austenitic Stainless  
Steel Weldments  
1981 Ultrasonics Symposium, Chicago, IL  
C. M. Fortunko  
October 14, 1981

Preparation of Ferrous Scrap Samples for Round Robin Testing  
ASTM, St. Louis, MO  
J. G. Early  
October 1981

Atomistic Aspects of Brittle Crack Propagation  
Materials Engineering Science Seminar, Virginia Polytechnic Institute  
and State University, Blacksburg, VA  
E. R. Fuller, Jr.  
November 10-11, 1981

Ultrasonic Nondestructive Evaluation of Girth Welds Using Electromagnetic-  
Acoustic Transducers  
The Welding Institute, Cambridge, England  
C. M. Fortunko  
November 14, 1981

Ultrasonic Nondestructive Evaluation of Girth Welds Using Electromagnetic-  
Acoustic Transducers  
AERE-Harwell, Oxford, England  
C. M. Fortunko  
November 16, 1981

Use of Conservation Integrals to Fracture Mechanics With Emphasis  
on Application of the J Integral to Assessment of Surface Defects  
The Welding Institute, Cambridge, England  
R. B. King  
November 16, 1981

Inspection of Stainless Steel Welds Using Horizontal Shear Waves  
Institut für Zerstörungsfreie Prüfverfahren, Saarbrücken, Germany  
C. M. Fortunko  
November 16, 1981

Fitness-for-Purpose Research at the National Bureau of Standards  
Fitness for Purpose Validation of Welded Constructions, London,  
England  
R. B. King  
November 17, 1981

Fracture Toughness of Steel Weldments for Arctic Structures  
U. S. Geological Survey Research and Development Seminar, Baltimore, MD  
H. I. McHenry  
November 18, 1981

Elastic Plastic Fracture Design Curves  
ASME Winter Annual Meeting, Washington, DC  
H. I. McHenry  
November 18, 1981

The Effect of Delta-Ferrite on the Mechanical Properties of Stainless  
Steel Welds at Cryogenic Temperatures  
American Society for Metals, New Orleans, LA  
T. A. Whipple  
November 18, 1981

Fitness-for-Purpose Research at the National Bureau of Standards  
AERE-Harwell, Oxfordshire, England  
R. B. King  
November 20, 1981

Screw Dislocation Screening and Fracture Criterion on Mode III  
Sharp Curve  
1981 New Orleans Topical Conference on Deformation, Fracture, Wear,  
and Nondestructive Evaluation of Materials: Physics and Practice,  
New Orleans, LA  
I.-H. Lin  
November 23, 1981

Ultrasonic Nondestructive Evaluation of Girth Welds Using Electromagnetic-  
Acoustic Transducers  
British Gas Research and Development Division, Northumberland,  
England  
C. M. Fortunko  
November 23, 1981

Atomistic Aspects of Brittle Cracking and Crack-Tip Chemistry  
Fall Meeting of American Physical Society, Topical Conference on  
Applications of Physics: Deformation and Fracture, New Orleans, LA  
E. R. Fuller, Jr.  
November 23-24, 1981

Ultrasonic Nondestructive Evaluation of Girth Welds Using Electromagnetic-  
Acoustic Transducers  
Krautkramer GMBH, Cologne, Germany  
C. M. Fortunko  
November 24, 1981

Nonmetallic Composite Applications in Advanced Energy Systems  
University of Illinois, Urbana, IL  
M. B. Kasen  
December 4, 1981



Fitness-for-Service of Pipeline Girth Welds  
NBS/DOT Workshop on Pipeline Girth Weld Standards, Boulder, CO  
R. P. Reed  
December 9, 1981

Detection and Sizing of Cracks Using Electromagnetic-Acoustic  
Transducers  
Case-Western Reserve University, Cleveland, OH  
C. M. Fortunko  
December 16, 1981

Lifetime Predictions for Brittle Materials  
Southwestern Section, American Ceramic Society, Albuquerque, NM  
S. W. Freiman  
December 1981

Ultrasonic Detection of Cracks Using Low Frequency Non-Contact  
Transducers  
Materials Advisory Committee: Non-Destructive Evaluation of Railroad  
Wheels, Pueblo, CO  
C. M. Fortunko  
January 5, 1982

Ship Steels for Improved Productivity  
AIME Annual Meeting, Dallas, TX  
H. I. McHenry  
February 16, 1982

The Effect of Delta-Ferrite on the Low Temperature Plastic Deformation  
of Austenitic Stainless Steels  
AIME Annual Meeting, Dallas, TX  
T. A. Whipple  
February 18, 1982

Stress Corrosion in Brittle Materials  
Seminar at Rutgers University, New Brunswick, NJ  
S. W. Freiman  
February 1982

The Establishment of Low Temperature Codes and Standards  
Metal Properties Council, Philadelphia, PA  
R. P. Reed  
March 4, 1982

Monitoring Stiffness Degradation in Graphite/Epoxy Composites  
1982 ASNT Spring Conference, Boston, MA  
R. D. Kriz  
March 24, 1982

Interim Round Robin Ferrous Scrap Test Data  
ASTM, Williamsburg, VA  
J. G. Early  
March 1982

Microdeformation Behavior of Beryllium  
JOWOG-82 Be Exchange at Rocky Flats National Laboratory, Rocky  
Flats, CO  
R. S. Polvani, C. S. Tilghman, and B. W. Christ  
April 19, 1982

EMAT's - A New Ultrasonic Noncontact Testing Technique  
Drexel University, Ultrasonic Seminar Series (G680-27),  
Philadelphia, PA  
C. M. Fortunko  
April 21, 1982

Creep Cavitation in Non-Uniform Stress Fields  
Graduate Seminar, Department of Mechanical Engineering and Mechanics,  
Lehigh University, Bethlehem, PA  
R. J. Fields  
April 31, 1982

Equivalency of Foreign and Domestic Material Specifications for  
Ships Components  
Society of Naval Architects and Marine Engineers, Washington, DC  
J. G. Early  
April 1982

The Effect of Cracks on the Reliability of Multilayer Capacitors  
National Materials Advisory Board, Washington, DC  
S. W. Freiman  
April 1982

Effects of Crack Growth on the Load-Displacement Characteristics of  
Precracked Specimens under Bending  
84th Annual Meeting of the American Ceramic Society, Cincinnati, OH  
T.-J. Chuang, E. R. Fuller, Jr. R. J. Fields and L. Chuck  
May 2-5, 1982

Stress Enhanced Crack Blunting  
84th Annual Meeting of the American Ceramic Society, Cincinnati, OH  
T.-J. Chuang, E. R. Fuller, Jr. and T. A. Michalske  
May 2-5, 1982

Comparison of Static and Dynamic Fatigue in  $Al_2O_3$   
84th Annual Meeting of the American Ceramic Society, Cincinnati, OH  
S. W. Freiman and A. C. Gonzalez  
May 2-5, 1982

Fracture of  $95PbZrO_3$ - $5PbTiO_3$   
84th Annual Meeting of the American Ceramic Society, Cincinnati, OH  
S. W. Freiman and J. J. Mecholsky  
May 2-5, 1982

Effects of Chemical Environments on Crack Growth in Soda-Lime Glass  
84th Annual Meeting of the American Ceramic Society, Cincinnati, OH  
S. W. Freiman and G. S. White  
May 2-5, 1982

Physics of Fracture  
Sosman Lecture, 84th Annual Meeting of the American Ceramic Society,  
Cincinnati, OH  
B. R. Lawn  
May 2-5, 1982

A Chemical Approach to Predicting Stress Corrosion Effects in  
Brittle Materials  
84th Annual Meeting of the American Ceramic Society, Cincinnati, OH  
T. A. Michalske and S. W. Freiman  
May 2-5, 1982

Crack Healing in Silica Glass  
84th Annual Meeting of the American Ceramic Society, Cincinnati, OH  
T. A. Michalske and E. R. Fuller, Jr.  
May 2-5, 1982

Analysis of Oxide : Matrix Interfaces in  $\text{Si}_3\text{N}_4$   
84th Annual Meeting of the American Ceramic Society, Cincinnati, OH  
N. J. Tighe  
May 2-5, 1982

Elastic-Plastic Fracture Mechanics Research at NBS  
Research Institute for Strength and Fracture of Materials, Sendai,  
Japan  
H. I. McHenry  
May 7, 1982

Magnetic Field Effects on Tensile Behavior of Fe-Cr-Ni Alloys at  
4 K  
International Cryogenic Engineering Conference/International Cryogenic  
Materials Conference (ICEC/ICMC), Kobe, Japan  
R. P. Reed  
May 11, 1982

Effect of Cryogenic Temperatures on the Mechanical Performance of  
Glass-Fabric Reinforced Epoxy and Polyimide Matrix Laminates  
International Cryogenic Engineering Conference/International Cryogenic  
Materials Conference (ICEC/ICMC), Kobe, Japan  
M. B. Kasen  
May 12, 1982

Stainless-Steel Elastic Constants at Low Temperatures: A Review  
International Cryogenic Engineering Conference/International Cryogenic  
Materials Conference (ICEC/ICMC), Kobe, Japan  
H. M. Ledbetter  
May 12, 1982

Mechanical Properties of Austenitic Stainless Steel Castings at 4 K  
International Cryogenic Engineering Conference/International Cryogenic  
Materials Conference (ICEC/ICMC), Kobe, Japan  
H. I. McHenry  
May 12, 1982



Low Temperature Flow Strength of Austenitic Stainless Steels  
International Cryogenic Engineering Conference/International Cryogenic  
Materials Conference (ICEC/ICMC), Kobe, Japan  
R. P. Reed  
May 12, 1982

Fracture Properties of 25-Mn Austenitic Steel and Its Welds at 4 K  
International Cryogenic Engineering Conference/International Cryogenic  
Materials Conference (ICEC/ICMC), Kobe, Japan  
H. I. McHenry  
May 13, 1982

Structural Alloys for Cryogenic Service  
International Cryogenic Engineering Conference/International Cryogenic  
Materials Conference (ICEC/ICMC), Kobe, Japan  
H. I. McHenry  
May 13, 1982

TEM Study of Indentation of Brittle Materials  
Symposium on Hardness, National Bureau of Standards, Washington, DC  
B. J. Hockey  
May 17-18, 1982

Elastic-Property Studies at NBS/Boulder  
University of Tokyo (Roppongi campus), Materials Science Department,  
Tokyo, Japan  
H. M. Ledbetter  
May 18, 1982

Fracture Mechanics Approach to Fitness-for-Purpose Standards  
American Welding Society Conference on Fitness-for-Purpose in  
Welded Construction, Atlanta, GA  
H. I. McHenry  
May 18, 1982

Low-Temperature Elastic-Constant Anomalies in Austenitic Stainless  
Steels  
Plasticity and Workability Section, Fundamental Research Laboratories,  
Nippon Steel, Kawasaki, Japan  
H. M. Ledbetter  
May 20, 1982

Dynamic Hardness Testing  
Microhardness-Related Research Symposium, National Bureau of Standards,  
Washington, DC  
R. S. Polvani  
May 25, 1982

Fracture Toughness of Piezoelectric Materials  
U.S.-Japan Workshop on Piezoelectric and Dielectric Ceramics,  
Tokyo, Japan  
S. W. Freiman  
May 1982

Lifetime Predictions for Ceramic Capacitors  
U.S.-Japan Workshop on Piezoelectric and Dielectric Ceramics,  
Tokyo, Japan  
S. W. Freiman and S. M. Wiederhorn  
May 1982

Fracture of Ferroelectric Materials  
U.S.-Japan Workshop on Piezoelectric and Dielectric Ceramics,  
Tokyo, Japan  
R. C. Pohanka and S. W. Freiman  
May 1982

Creep Cavitation and Fracture due to a Stress Concentration in  
2½ Cr-1Mo Steel  
2nd International Symposium on Defects, Fracture and Fatigue,  
Quebec, Canada  
T.-S. Liu, T. J. Delph, and R. J. Fields  
June 1, 1982

In-Process Weld Inspection for New Construction  
Interdisciplinary Program for Quantitative Nondestructive Evaluation,  
Iowa State University/Navy/DARPA, Ames, IA  
C. M. Fortunko  
June 2, 1982

Environmental Testing Under Conditions that Promote Branch Crack  
Forman in Double Beam Specimens  
Third International Conference on Hydrogen and Materials, Paris,  
France  
C. G. Interrante  
June 10, 1982

Fracture Mechanics Applications to Failure Analysis and Prevention  
in Structures and Components  
Centro Informazioni Studi Esperienze, CISE, Milan, Italy  
C. G. Interrante  
June 14, 1982

Testing Cements in the Cerro Prieto Geothermal Field  
API Standardization Conference, Colorado Springs, CO  
R. F. Krause, Jr.  
June 14, 1982

Hyatt Regency Skywalk Collapse  
CBT Failure Analysis Workshop, National Bureau of Standards,  
Gaithersburg, MD  
T. R. Shives  
June 1982

Fracture of Ceramic Capacitors  
Seminar at Japanese National Defense Academy, Yokosuka, Japan  
S. W. Freiman  
June 1982

Contact Fracture in Brittle Materials  
International Symposium on Contact Mechanics and Wear of Rail/Wheel  
Systems, University of British Columbia, Vancouver, Canada  
S. M. Wiederhorn and B. R. Lawn  
July 6-9, 1982

The Residual Strength Diagram Based on the Plastic Yield Strip  
15th ASTM National Symposium on Fracture Mechanics, College Park,  
MD  
R. de Wit  
July 7, 1982

Post-Yield Crack Opening Displacement for Surface Cracks in Tensile  
Panels  
15th ASTM National Symposium on Fracture Mechanics, College Park,  
MD  
D. T. Read  
July 7, 1982

Microscopy of Erosion  
MICRO '82, International Symposium on the Use of Microscopy in  
Studying Materials Degradation, London, England  
B. J. Hockey  
July 12-16, 1982

Some Recent Developments in Indentation Fracture  
MICRO '82, International Symposium on the Use of Microscopy in  
Studying Materials Degradation, London, England  
B. R. Lawn  
July 12-16, 1982

Excitation of Pure Ultrasonic Modes with Electromagnetic-Acoustic  
Transducers  
AISI, DARPA, NBS Workshop on Process Control for the Steel Industry,  
Gaithersburg, MD  
C. M. Fortunko  
July 28, 1982

Use of Electromagnetic-Acoustic Transducers in Weld Inspection  
U.S. Navy, NAVSEA, Materials Branch, Crystal City, VA  
C. M. Fortunko  
July 28, 1982

Nondestructive Evaluation of Thick Weldments Using Arrays of  
Electromagnetic-Acoustic Transducers  
DARPA-AF Review of Progress in Quantitative NDE, La Jolla, CA  
C. M. Fortunko  
August 2, 1982

SRMs for Determination of Retained Austenite in Hardened Steels  
31st Annual Conference on X-ray Analysis, Denver, CO  
G. E. Hicho  
August 5, 1982



Dislocation Processes at Crack Tips  
Gordon Research Conference on Solid State Studies in Ceramics,  
Plymouth, NH  
R. M. Thomson, E. R. Fuller, Jr., and I.-H. Lin  
August 9, 1982

Long-term Fracture Phenomena of Structural Ceramics  
Gordon Research Conference on Solid State Studies in Ceramics,  
Plymouth, NH  
R. J. Fields  
August 9-13, 1982

#### Division Seminars

Statistical Theory of Physical Properties of Random Media  
Ekkehart Kröner  
Institute for Theoretical and Applied Physics, University of Stuttgart,  
Stuttgart, West Germany  
October 19, 1981

Fracture Mechanics Analysis of Pipeline Welds  
M. G. Dawes  
The Welding Institute, London, England  
October 20, 1981

Elastic Properties of Textured Metals  
H. M. Ledbetter  
Division 562, NBS/Boulder  
October 27, 1981

Gauge-Invariant Formulation of the Continuum Theory of Defects  
G. K. D. Gairola  
Institute for Theoretical and Applied Physics, University of Stuttgart,  
Stuttgart, West Germany  
January 12, 1982

Fracture Mechanics Analysis of Surface Flaws in Pipeline Girth  
Welds  
R. B. King  
Division 562, NBS/Boulder  
January 18, 1982

Degradation of Composites by Moisture Absorption  
R. D. Kriz  
Division 562, NBS/Boulder  
February 1, 1982

Studies of Elastic-Plastic Fracture Using Dislocation Theory  
I.-H. Lin  
Division 562, NBS/Boulder  
February 16, 1982

NDE Research by EPRI  
Mel Lapidès  
Electric Power Research Institute (EPRI), Palo Alto, CA  
February 26, 1982

New Experimental Capabilities in the Fracture and Deformation  
Division

J. C. Moulder  
Division 562, NBS/Boulder  
March 1, 1982

COD of Surface Flaws in Pipeline Girth Welds

Y.-W. Cheng  
Division 562, NBS/Boulder  
March 15, 1982

Properties of Stainless Steel Castings at 4 K

T. A. Whipple  
Division 562, NBS/Boulder  
March 29, 1982

Magnetoelastic Properties of Austenitic Stainless Steels at Low  
Temperatures

H. M. Ledbetter  
Division 562, NBS/Boulder  
April 12, 1982

Microdeformation Behavior of Beryllium

R. S. Polvani, C. S. Tilghman, and B. W. Christ  
Division 562/NBS Boulder  
April 21, 1982

Fundamentals of Grain Boundary Segregation

M. B. Kasen  
Division 562, NBS/Boulder  
April 26, 1982

Ultrasonic Wave Propagation in Random and Periodic Particulate  
Composites

Vikram K. Kinra  
University of Colorado, Department of Mechanical Engineering,  
Boulder, CO  
May 5, 1982

Use of Small Scale Indentation Flaws to Study Fatigue Properties of  
Glass

T. P. Dabbs  
School of Physics, University of New South Wales, Kensington,  
Australia  
May 7, 1982

Flaw Detection and Weldments by EMATs and Possible Signal Processing Techniques

R. E. Schramm

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May 10, 1982

Design of Electrical Coupling Networks for Acoustic Transducers with Compact Responses

Dov Hazony

Case-Western Reserve University, Cleveland, OH

May 13, 1982

Using EMATs for Stress Measurement and Weld Inspection

G. A. Alers

Magnasonics, Inc., Albuquerque, NM

May 20, 1982

Analytical Methods in Eddy Current NDE

Professor B. A. Auld

Stanford University, Stanford, CA

May 31, 1982

Small-Angle Neutron Scattering Study of Grain Boundary Cavitation

M. H. Yoo

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN

June 14, 1982

Direct Observations of Crack-Tip Dislocations in Metals

S. M. Ohr

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN

June 15, 1982

Testing Cements in the Cerro Prieto Geothermal Field

R. F. Krause, Jr.

Division 562, NBS/Boulder

June 16, 1982

Chemical Effects on Ceramic Fracture

T. A. Michalske

Sandia National Laboratories, Albuquerque, NM

June 25, 1982

Standard Reference Materials for Determination of Retained Austenite in Hardened Steels

G. E. Hicho

Division 562, NBS/Boulder

August 4, 1982



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Kiandra/Talisman Lodge, Vail, CO  
October 1981

ONR-NBS Workshop on Contact Damage in Ceramic Materials at Elevated Temperatures  
National Bureau of Standards, Gaithersburg, MD  
January 21-22, 1982

Mechanical Failures Prevention Group Symposium on Time-Dependent Failure Mechanisms and Assessment Methodologies  
National Bureau of Standards, Gaithersburg, MD  
April 20-22, 1982

Seventh International Symposium on Ultrasonic Imaging and Tissue Characterization  
National Bureau of Standards, Gaithersburg, MD  
June 6-9, 1982

#### Consulting and Advisory Services

DARPA, AISI, and NBS advisory workshop on sensors for steel industry  
C. M. Fortunko

Electric Power Research Institute  
C. M. Fortunko

Lawrence Livermore National Laboratory  
C. M. Fortunko

Rockwell International Science Center  
C. M. Fortunko

U. S. Army, ARRADCOM  
C. M. Fortunko

U. S. Navy, DTNSRDC  
C. M. Fortunko

NBS Research Advisory Committee to Dr. E. Ambler  
E. R. Fuller, Jr.

Gas Research Institute, International Steering Committee on Cryogenic 9 Percent Nickel Steel  
H. I. McHenry

Consultation on material properties at low temperatures for large superconducting magnet structures being built in the U.S., (General Dynamics, General Electric, Westinghouse, Lawrence Livermore Labs., Oak Ridge National Lab.), Japan, Germany, and Switzerland  
R. P. Reed

Department of Energy, Office of Fusion Energy, Research Advisory Committee  
R. P. Reed

Metal Properties Council, Technical Advisory Panel  
R. P. Reed

National Science Foundation, Materials Research Advisory Committee, Metals, Ceramics, Polymers, and Metallurgy Oversight Committee  
R. P. Reed

#### External Recognition

Degradation of Materials III: Toughening and Fracture Toughness  
Fall Meeting of the Metallurgical Society and the Basic Science  
Division of the American Ceramic Society, Louisville, KY, Co-chairman  
October 12-15, 1981  
E. R. Fuller, Jr.

Doctoral Advisory Committee of Murari Singh, New York State College  
of Ceramics at Alfred University, Honorary Member  
June 1982  
E. R. Fuller, Jr.

Sosman Lecture Award  
American Ceramic Society  
B. R. Lawn  
1982

Fitness-for-Purpose Validation in Welded Constructions Conference,  
Vice-Chairman  
May 1982  
H. I. McHenry

International Cryogenic Materials Conference, Kobe, Japan, Session  
Chairman  
May 1982  
R. P. Reed, H. I. McHenry, and M. B. Kaşen

TECHNION, Israel Institute of Technology  
Invited Professor  
September-October 1981  
S. M. Wiederhorn

## Industrial Interactions

Joint development program of low temperature structural austenitic steel, Armco Steel, Middleton, OH, R. P. Reed

Joint characterization of low temperature properties of structural alloys, Kawasaki Steel, Nippon Steel, Kobe Steel, Nippon-Kokan Steel, Japanese Steel Works, DOE (Office of Fusion Energy), and NBS, R. P. Reed and H. I. McHenry

Development of low temperature codes and standards, joint research effort, includes development of test methodology, round-robin testing, and development of materials specifications, Metal Properties Council (ASTM, ASME, ASM, AWS), DOE (Office of Fusion Energy), NBS, and about 20 companies, R. P. Reed

Development of fitness-for-purpose criteria for proposed Alaska Natural Gas Pipeline, joint research and collaboration, NBS, Welding Research Council, Northwest Pipeline Company, Exxon, Nova, and Canadian Welding Research Council, R. P. Reed, M. B. Kasen, C. M. Fortunko, and H. I. McHenry

Possible use of electromagnetic-acoustic transducers in nondestructive evaluation, Panametrics, Inc., Waltham, MA, C. M. Fortunko

Measurement of residual stresses and inspection of residual stresses and inspection of weldments using electromagnetic-acoustic transducers, Magnasonics, Inc., Albuquerque, NM, C. M. Fortunko

Nondestructive evaluation of stainless steel weldments, Battelle/Northwest Laboratories, Richland, WA and Argonne National Laboratory, Chicago, IL, C. M. Fortunko

Thickness gaging of tubular goods, Republic Steel, Cleveland, OH, C. M. Fortunko

In-service monitoring in nuclear industry, AMDATA, Inc., San Jose, CA, C. M. Fortunko

Design of circuits for nondestructive evaluation, Rockwell International Science Center, Thousand Oaks, CA, C. M. Fortunko

Participation in round-robin fracture mechanics prediction of heavy section structural testing pressure vessel test, Oak Ridge National Laboratories, Oak Ridge, TN, D. T. Read

Refinement of the manufacturing specifications for the G-10CR cryogenic grade of insulating nonmetallic laminate with the Spaulding Fiber Co., Tonawanda, NY, Westinghouse Industrial Laminates Corp., Hampton, SC, Synthane-Taylor Corp., Oaks, PA, NVF Corp., Kenneth Square, PA, and the Norplex Corp., LaCrosse, WI, M. B. Kasen



## POLYMER SCIENCE AND STANDARDS DIVISION (563)

Ronald K. Eby, Chief  
Martin G. Broadhurst, Deputy Chief  
B. A. Hyde, Secretary

Although synthetic polymers have been used as materials for technology during only three quarters of a century, they have left little of our economy, technology, industry, science, and culture untouched. We have moved rapidly into an age in which an evergrowing number of humanity's needs are served by polymers. The volume currently produced exceeds that of steel and forms the basis of industries which add over \$90 billion of value by manufacturer (a measure of the relative economic importance of manufacturing among industries) and provide 3.4 million jobs. Recent summaries show that polymers and polymer composites research already accounts for about 47 percent of the total industrial R&D expenditure for metals, polymers, and inorganic materials. Among these materials, polymers also constitute about 39 percent of the value added by manufacturer, 49 percent of the jobs, 45 percent of the number of scientific publications, and 39 percent of the American Society for Testing and Materials (ASTM) standards.

Polymers have been shaped by intellectually sophisticated research which has been recognized by a number of Nobel Prizes. The resulting materials have contributed to national industrial productivity through their economy, ease of fabrication, and useful properties such as low density, corrosion resistance, and toughness. Polymers are energy efficient; the largest volume polymer, polyethylene, uses 29 percent of the energy per unit volume required by steel for conversion from raw to refined material and yields further savings in processing and shipping. In fact, studies have shown that for every barrel of oil used to make plastic products, approximately one barrel is saved in comparison with the use of the next best alternative material. These useful properties have enabled polymers to contribute to increased national economic strength both by creating entirely new products and by substituting for other materials in existing products.

Polymers have entered a widening range of increasingly sophisticated and demanding applications. Polyvinylidene fluoride films are used as piezoelectric transducers in high fidelity sound systems. Structural parts of aircraft are constructed from composites with a polymer matrix and sometimes a polymer reinforcement. Polyurethane elastomers are used to pump blood in circulatory assist devices. The list of such examples is very long, and includes trends for the increased use of polymers in packaging, construction, transportation, national security, electronics, information handling, clothing, electrical appliances, energy, dentistry and medicine. Since polymer science and technology is on the steep part of the learning curve, these trends create many new needs for scientific concepts, measurements, standards, and data that can be used to ensure their reliable performance in the use, processing, and other phases of the material cycle. The programs of the Division are aimed at the fundamental scientific basis of these needs.

To identify the key needs with the best prospects for payoff, the managers of the Polymer Science and Standards Division make structured visits to industrial and Government laboratories. Visited sites include Bell Laboratories, E. I. DuPont de Nemours, Inc., Johnson and Johnson, Army R&D Command, General Motors Corporation, Boeing, and Lawrence Livermore Laboratories. Surveys have been conducted in the areas of durability, composites, and processing. These and other contacts with research associates, experts in industry, trade associations, standards associations, guest workers, Government, and academia ensure that the Division's efforts are directed toward fostering the effective use of polymers in solving generic national problems. These include the growth of the economy, national security, efficient Government, materials utilization, and conservation of critical materials.

Current activities are associated into areas concerned with long-term research on the scientific basis for mechanical reliability in load-bearing applications, chemical durability, lifetime prediction, migration of protective additives, characterization methods, standards for molecular composition and performance properties, dielectric properties, processing and reliability of composites, and reliable dental and medical materials. Substantial cooperative efforts are conducted with research associates from a number of industries, universities, the Department of Defense, the National Institutes of Health, the American Dental Association (ADA), the Food and Drug Administration, and the Bureau of Engraving and Printing. All these efforts lead the staff of the Division into an examination of the scientific basis of those properties which are of concern to people who use, design, and produce useful polymer objects. This work helps society capture, in safe and satisfying ways, the benefits of the increasingly widespread application of polymers.

#### FY82 SIGNIFICANT ACCOMPLISHMENTS

##### POLYMER STANDARDS FOR PROCESS CONTROL AND EQUITY Task 12132

- Construction of a selfcalibrating gel permeation chromatograph (GPC) has been completed. A light scattering detector for the GPC measures, in real time, the scattering intensity of the effluent as a function of scattering angle. This allows immediate identification of difficulties such as molecular association, microgel formation, etc. which affect the validity of the molecular weight determinations. This instrument will be utilized for the more rapid characterization of new polymer molecular weight standards.
- A high performance liquid size exclusion chromatograph laboratory has been established for the determination of the molecular weight and molecular weight distribution of polymer samples. The apparatus has been automated and may be operated at temperatures up to 150 °C, the temperature required for the dissolution of polyethylene and certain other crystalline polymers. Graphics and database capabilities are built into the software to allow the user easy interpretation of the data once it is collected.



- The certification of Standard Reference Material 1470 for transmission of helium, carbon dioxide, oxygen, and nitrogen gases has been completed. Gas transport properties of polymeric materials are the major determinant of suitability for end use in a great variety of applications ranging from food and beverage packaging, industrial gas separation processes, and sterilization of medical devices, to substrates and packages for semiconductor products. Gas molecules are useful as probes of materials properties at the microstructural level.
- Polymer properties can be greatly altered by controlling the size and shape of the phase separated domains of polymer blends and copolymers. In collaboration with Dr. H. Hasegawa of Kyoto University, we have prepared model systems of polystyrene-polyisoprene which have regular lamellar domains. Dimensions of the deuterium labeled polystyrene block of this diblock copolymer and the dispersed homopolystyrene molecules have been measured at different directions relative to the domain orientations by small angle neutron scattering (SANS). Work on the characterization of blends by SANS is being carried out in collaboration with a Research Associate from Exxon.
- A new statistical mechanical model for a chain liquid has been developed which shows a solid-liquid transition as well as a liquid-vapor transition. This work is being carried out in collaboration with R. H. Lacombe of IBM (Fishkill). This model may prove to be useful in describing the phase behavior of polar polymer blends.
- A new instrument for forced Rayleigh light scattering is being completed. A split laser beam is recombined at a small crossing angle on a sample which includes a trace of polymer labeled with a photochromic dye. This beam is pulsed to produce an interference pattern which bleaches a holographic grating in the sample. A second laser beam is diffracted by the grating. As the labeled polymers diffuse, the grating is destroyed. Thus, measuring the intensity decay of the diffracted beam yields the diffusion coefficient of the labeled species. Since the distance scale is typically several orders of magnitude smaller than macroscopic tracer methods, it is possible to measure extremely small diffusion coefficients such as those expected for polymer molecules in concentrated solutions and melts.

#### TESTS, STANDARDS, AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS

Task 12135

- A silver staining technique developed for investigating wear damage in dental composites was applied to assessment of micro-leakage and composite restorations and increased precision relative to a more laborious radioisotope ( $\text{Ca}^{45}$ ) technique was demonstrated.



- A promising new monomer type, polythiols, was introduced to the dental materials research community. A high molecular weight, moderately viscous polythiol, pentaerythritol tetra (3-mercaptopropionate), has promise for reducing residual unsaturation and polymerization shrinkage in dental composites.
- Developed a procedure employing coupling agents and a mineralization step that achieves a degree of stable bonding to dentin approximately three times that hitherto reported. As a result, the potential exists for improved clinical treatment of erosion, root caries and other conditions by reducing the amount of dentin that needs to be cut for mechanical retention.
- Several new dental cement innovations were introduced to the dental materials research community. Arousing particular dental profession and industry interest is a cement formulation based on hexyl vanillate, ethoxybenzoic acid and zinc oxide. Low water sorption, high strength, non-inhibiting to free radical polymerization of subsequently applied composites or resins and predictably good tissue tolerance are important characteristics of this new cement.
- Silver staining and small angle x-ray scattering analysis of removed clinical composite restorations have been used to define mechanisms of wear. In the laboratory a softening of the composite resin matrix by a range of food-simulating solvent media has been shown to produce similarly damaged materials. This information has permitted appropriate modification of in vitro testing and resulted in emphasizing the crucial importance of the degree of cure in the composite polymer.
- Fourier Transform Infrared has been used to demonstrate the extent of under cure of dental composite resin matrices achieved at oral temperatures relative to that reached at higher temperatures. A higher degree of cure is obtained by building more polymer backbone flexibility into the monomer formulation indicating a viscosity controlled process. These results provide important guides for laboratory testing and developmental directions of the dental industry.
- Research pin-pointed food debris and oral liquid interactive softening of dental composite restorations as initial steps in clinical loss of restoration material. Based on these results, an erosion (high velocity liquid jet) test was designed and assembled. SEM examination of composite surfaces exposed to the test revealed surface deterioration similar to that experienced clinically. The test in conjunction with other wear test procedures is expected to provide industry and other research groups with an important assist in development of more durable composite restorations.
- A new concept for evaluation of porcelain-metal bond strengths has been developed. The test uses four-point bending of a metal strip to which porcelain is fused and measures a tensile strength

without influence from shear stresses. Three dental manufacturers have sent personnel to develop a first hand experience with the test procedure which is anticipated to be useful in industrial examinations of porcelain-alloy combinations and as a specification test method.

- Amines have been shown in this laboratory to be more reactive with the resin, BIS-GMA, than current commercial materials. They have now also been shown to be useful for upgrading surgical bone cement. These amines in conjunction with a substitution of dicyclopentyloxyethyl methacrylate for the presently used methyl methacrylate give a faster cure with less liberation of heat.
- Characterization of the porosity in low modulus porous polymeric materials designed for medical and dental implant purposes is important for establishing a correlation of porosity and the implant stabilizing tissue or bone ingrowth. Mercury intrusion, BET surface area and quantitative stereology measurements have been made. The nature of the porosity characteristics as determined by each technique is being defined.

#### MECHANICAL DURABILITY OF POLYMERS

##### Task 12136

- Carbonyl concentrations have been determined by FTIR for fatigued ultra high molecular weight polyethylene as a function of number of cycles, frequency and peak stress level. The results suggest that mechanical failure occurs at a particular concentration of carbonyls. The measurement of carbonyl concentration may form the basis of an NDE method.
- Carbon -13 NMR techniques have been developed to elucidate molecular structure of ultra high modulus polymeric materials. The fraction of material in the form of molecules that bridge one crystalline lamella to another has been determined. Bridge molecules are thought to be responsible for the high tensile properties and the quantitative NMR determinations can be used to evaluate the effects of processing conditions on the molecular arrangements. This technique is being applied to high strength poly(ethylene terephthalate) fibers in a joint project with the Firestone Tire & Rubber Co.
- A new improved test method for environmental stress crack resistance of ethylene-based plastics has been developed. The method has the advantages of a reduction in the time required to carry out the test, and a reduction of experimental scatter in the data. A description of the test method and a summary of test results, including the appropriate statistical data, has been presented to Committee D-20.12.03 of the ASTM.
- A viscoelastic relationship has been developed that is capable of describing quantitatively both creep and recovery behavior

of polymeric materials which have not been mechanically preconditioned. Previous theories could be applied successfully only to materials that were first mechanically conditioned and thus the mechanical behavior of as-processed materials could not be adequately predicted.

- The creep and stress relaxation behavior of ultra high molecular weight polyethylenes used in synthetic implant applications has been determined as a function of molecular weight and various thermal treatments. Electron microscopic investigations of deformed specimens have shown that preferential deformation occurs at boundaries which delineate the interfaces between the sintered grains of raw polymer.
- A torsional dilatometer has been designed and constructed to determine the effects of torsion on the volume of polymer glasses. The data will serve to test theories concerning the behavior of polymer glasses under deformation and the effects of deformation on the aging of these materials.

#### PROCESSING AND RELIABILITY OF POLYMER COMPOSITES Task 12137

- A failure model has been developed and applied to elastomer modified epoxy formulations. The temperature dependence of the fracture energy could be described with a single Arrhenius type activation energy whose value was identical to that obtained from yield experiments. This provides the first direct evidence that yielding is a crucial step in the toughening mechanism of elastomer modified epoxy resins systems used in aerospace applications.
- A joint program involving NASA, Hercules, Hexcel, the University of Illinois, and NBS is addressing the need for test procedures to assess the susceptibility of polymer composites to delamination. Delamination is a major concern in the mechanical reliability of continuous-fiber reinforced composites. Results during the past year have led to guidelines for the design of test specimens in terms of size, geometry, and lay-up (the sequence of fiber layers and their orientation).
- A research associate from Martin Marietta Corporation, spent six months at NBS applying Fourier transform infrared spectroscopy (FTIR) to characterization of the processing of composites used in the Space Shuttle Program. Results indicated that IR spectroscopic data could be used to improve the processibility of composites.
- A model has been developed to analyze small angle x-ray data of particulate composites in terms of three phases: the polymer matrix, the particulate reinforcement, and microcracks or voids. From this model the content and characteristic lengths of microcracks or voids can be determined from the angular dependence



of the x-ray scattering intensities. The method provides a means of assessing the state of damage of particulate-reinforced composites.

- An ultrasonic test method has been developed to study the curing process (the liquid to solid conversion) in thin layer films. The method will provide a better understanding of the chemistry of processing thermoset polymers and more reliable mechanical properties data of polymer matrix materials.
- A spectroscopic technique has been developed to monitor the chemical reactions that occur during processing polymer composites and subsequent to processing (post-cure). Using this technique the effects of initiator type and concentration as well as the molecular flexibility of the prepolymers have been investigated. The degree of post-curing was found to be affected primarily by the molecular flexibility of the prepolymer.

#### ADDITIVE MIGRATION AND CHEMICAL DURABILITY OF POLYMERS

##### Task 12138

- Kinetic data on the production of acidic groups in the hydrolysis of crosslinked polyester polyurethanes and polyethylene terephthalate have been measured. These data are being used in kinetic schemes recently developed at NBS to predict the lifetimes of these polymers when used as base materials and magnetic tape binders to store archival information. The information provides far more realistic estimates of when archival material should be recopied.
- Thermal degradation occurs during the processing stage for many polymer-based materials. Activation energies and a kinetic scheme for thermal degradation have been provided for polyisobutylene using a thermogravimetric technique developed at NBS. The important effect of pressure on volatile production and on the measured kinetic values used to estimate the extent of thermal degradation has been demonstrated by means of calculation and experimental data. New thermogravimetric techniques have been developed which greatly ease the characterization of degradation mechanisms.
- The relative contributions of thermal and photolytic degradation in PMMA used as solar cover plate materials are being elucidated by first exposing the materials to controlled environments and then determining the molecular weight as a function of depth in a series of highly precise measurements. The contributions of other factors to the degradation will be examined in a continuing series of experiments. The aim is to predict molecular weight changes as a function of exposure. This will make it possible to estimate changes in mechanical properties with exposure.
- Highly sensitive fluorescence techniques have been developed to provide measurements on migration rates, and have been applied

to: (1) measurement of the migration rate of an amine antioxidant from low density polyethylene, and (2) translation diffusion of chain molecules in semi-dilute solution. The second area provides data needed for tests of the scaling and reptation concepts proposed by de Gennes.

- An inverse phase gas chromatographic technique has been developed and applied to the measurement of diffusivities of several migrants in high density polyethylene. Such data are used in modelling the rate of loss of plasticizers and stabilizers from polymeric materials.

#### MICROSTRUCTURE AND PERFORMANCE OF DIELECTRIC PLASTICS

##### Task 12139

- A new time domain dielectric spectrometer has been developed. It rapidly measures and transforms charge-time data to dielectric constant and loss as a function of frequency over the range from  $10^{-3}$  to  $10^5$  Hz. This measurement technique, which meets an industrial need for rapid and accurate measurement over a wide frequency range, will be adapted for industrial use by a Research Associate from G.E.
- A major review of data and mechanisms for dielectric loss in materials at microwave frequencies was prepared for the U.S. Army Civil Engineering Research Laboratory. This data is needed to better understand and control the reflection of microwaves from solid structure.
- A ferroelectric to paraelectric transition in a copolymer of vinylidene fluoride and trifluoroethylene was shown to be due to a change in conformation of the chain within the crystal phase of the polymer. Such conformational changes have important implications on the long-term, high temperature durability of piezoelectric polymeric transducers. This work was done in a cooperative project with Bell Laboratories.
- The NBS-perfected technique for measuring space charge and polarization distribution in a thin polymer film has been successfully applied to electron-beam charged PVC and to PVDF after reversal of the poling field. Polymer-charge interactions leading to nonuniform electric fields are believed to play a key role in the performance of insulating materials.
- The use of polyvinylidene fluoride piezoelectric and pyroelectric transducers at elevated temperatures is limited to about 100 °C due to loss of polarization although the melting point of the polymer is near 170 °C. A rapid method for measuring pyroelectric response as a function of temperature has been developed as a first step in determining the variables which influence this loss in order to provide the basis for improved high temperature performance. This work was done in collaboration with the Brown Research Foundation.

- The processing conditions required to produce thick films of polyvinylidene fluoride transducers for sensitive hydrophones were successfully demonstrated to the Naval Ocean Systems Command. These thick films are most promising for hydrophone applications.
- Piezoelectric polymer sensors produced at NBS are being evaluated as monitors in cardiac patients in collaboration with the CNR Institute of Clinical Physiology.
- With support from the Office of Naval Research, NBS has initiated a long-range investigation into the relation between morphology and structure of polymers and the highly specific property of fast ion transport. These types of polymers have potentially high payoff applications as solid state electrolytes in batteries and fuel cells and as highly specific electrochemical sensors.
- At the request of the Department of Energy, an NBS evaluation has shown that electrical resistivity changes in cellulose acetate after neutron irradiation would not be useful as an effective neutron dosimeter. This conclusion is contrary to a report published by another laboratory.

In the following pages, the activities of the Division are presented formally in six tasks, each described separately:

12132 POLYMER STANDARDS FOR PROCESS CONTROL AND EQUITY

12135 TESTS, STANDARDS, AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS

12136 MECHANICAL DURABILITY OF POLYMERS

12137 PROCESSING AND RELIABILITY OF POLYMER COMPOSITES

12138 ADDITIVE MIGRATION AND CHEMICAL DURABILITY OF POLYMERS

12139 MICROSTRUCTURE AND PERFORMANCE OF DIELECTRIC PLASTICS.



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## POLYMER STANDARDS FOR PROCESS CONTROL AND EQUITY Task 12132

This task provides standard reference materials (SRMs) to the \$30 B/year synthetic polymers producing industry. Molecular weight SRMs are used extensively in industry to calibrate gel permeation chromatographs (GPCs) which are used routinely to measure polymer molecular weights and molecular weight distributions. The latter are the most important physical feature in determining a polymer's processability and its ultimate performance. Gas transmission and rubber SRMs are used in process control applications.

Improved characterization techniques are essential to providing improved SRMs. A fundamental knowledge of polymer solution properties such as osmotic pressure, viscosity, diffusional behavior, and scattering power is essential to this goal. As a consequence, a majority of the activities in this task involve experimental and theoretical studies of polymer solution properties. As a spinoff of our characterization activities, this task also provides data and concepts which are useful in polymer processing.

The execution of this task was assisted by Dr. D. Lohse, an industrial research associate from Exxon, Dr. J. G. Dillon, a guest worker from the Food and Drug Administration, and A. Z. Akcasu, a guest worker from the University of Wisconsin.

### Self-Calibrating Gel Permeation Chromatography Subtask 1 of Task 12132

P. H. Verdier

Gel permeating chromatography is a widely accepted technique for estimating the molecular weight distribution (MWD) of high polymers. However, the usefulness of the conventional GPC apparatus is limited by the need to provide calibrants for each polymer measured of known molecular weight over the entire molecular weight range in which the MWD is significantly different from zero. The calibration depends, among other things, upon the chemical nature, degree of branching, etc., of the polymeric material so that each new material requires a fresh calibration. The so-called "universal calibration" hypothesis, while useful, is limited to comparisons of polymers of similar shape and, in any event, is inadequate for quantitative determinations. Some instruments, one of which is commercially available, attempt to circumvent the need for calibrants by adding a single-angle light scattering detector to the usual concentration-sensitive detector. However, this does not allow the extrapolation to zero scattering angle which is required, in principle, to relate scattering intensity to molecular weight. In addition, qualitative information on the variation of scattering with angle, normally required to give assurance that meaningful results are being obtained, is not available.

We are designing and constructing a light scattering detector for the GPC which measures, in real time, the scattering intensity as a function of scattering angle and which is controlled by a dedicated minicomputer

in a way that allows scattering to be measured as a function of scattering angle and concentration. The instrument will allow continuous monitoring of the variation of scattering with angle. This will allow immediate identification of difficulties such as association, microgel formation, etc., which could affect the validity of the molecular weight obtained, an important consideration for work on new and unstudied materials. In addition to molecular weight, the mean-square radius (radius of gyration) will be obtained as a function of molecular weight, at least in the higher ranges of molecular weight, providing useful information for the characterization of branched polymers.

We expect to complete construction of the instrument by the end of FY82. In the coming year, we will start making measurements with it and developing procedures for high-quality molecular weight determinations.

#### Liquid Size Exclusion Chromatography Subtask 2 of Task 12132

H. L. Wagner and J. D. Barnes

A commercial high performance liquid size exclusion chromatograph has been installed for the determination of the molecular weight and molecular weight distribution of polymer samples. The apparatus has been automated and may be operated at temperatures up to 150 °C, the temperature required for the dissolution of polyethylene and certain other crystalline polymers. The unit is self-contained so that as many as 16 samples may be prepared internally. The conditions for each sample may be programmed separately and as many as nine replicate injections are possible. In conjunction with the automated data acquisition system, it is possible to run for over a 24 hour period without operator attention. The actual time required will depend on the columns and time allowed between runs for sample preparation and data acquisition.

The software has been designed so that the user does not need to learn the operating system of the computer and so that there is a one-to-one correspondence between the data required to program the chromatograph (which is microprocessor controlled) and that required to perform data analyses in the computer. Graphics and database capabilities are built into the software to allow the user easy interpretation of the data once it is collected.

This facility will be employed for many of the problems encountered in the Polymer Science and Standards Division where molecular weight distribution is a controlling variable. Changes in molecular weight distribution have been found to correlate with changes in many physical properties such as tensile strength, modulus, relaxation times, elongation, and stress cracking. The equipment has already been employed successfully in support of a project for the NBS Center for Building Technology involving the affect of ultraviolet exposure on polymethyl methacrylate.



Limiting Viscosity Number of Ultrahigh Molecular Weight Polyethylene  
Subtask 3 of Task 12132

H. L. Wagner and J. G. Dillon

Limiting viscosity number (intrinsic viscosity) measurements are required for the specification and control of ultrahigh molecular weight polyethylene (UHMWPE), one of the most extensively employed surgical implant materials. Because the viscosity number is dependent on shear rate, it should be measured at zero or very low shear rates where this dependency does not occur. For this purpose a low shear rate viscometer capable of being operated at high temperatures (135 to 145 °C) was constructed. The problems associated with the viscometer and some of the measurement difficulties, described in previous reports, have been overcome.

This type of viscometer is not commercially available and requires more than routine skill for its operation. However capillary viscometers, in which the shear rate can be quite high, have been successfully employed for many years for lower molecular weight polymers which are not sensitive to shear rate. A set of experiments were performed in which the same solutions, fraction of UHMWPE, were measured in decalin at 135 °C in both the low shear viscometer and a commercial capillary viscometer which is of a standard design. As shown in figure 1 an empirical relation exists between the two, so that a routine capillary viscometer measurement may be used to estimate the low shear value provided the capillary viscometer is of the same capillary size and volume as used in these experiments.

The measurements were made on fractions of UHMWPE obtained by the method described below. In order to assure complete dissolution of these fractions it was necessary to cut the material into 1/2 mm bits and to heat in decalin at 180 °C under nitrogen for one hour, with occasional gentle mixing to prevent agglomeration of the bits. This method was successful with all but the highest molecular weight fraction. The poor reproducibility of the results for this fraction, where viscosity numbers were of the order of 60 dl/g, indicates that solution was incomplete. From 4 to 8 measurements were made for each of 10 fractions to determine the limiting viscosity number of each fraction. These ranged from 9 to 52 dl/g.

These or similar fractions will be used to obtain the relationship between molecular weight and viscosity numbers by light scattering for these very high molecular weight polyethylenes. The Mark Houwink relation between viscosity and molecular weight, obtained empirically for lower molecular weight polymers, is not expected to hold for UHMWPE. When this relation is available, it should be possible to obtain molecular weights from simple capillary viscosity measurements in a standard viscometer.

Fractionation of Ultrahigh Molecular Weight Polyethylene  
Subtask 4 of Task 12132

H. L. Wagner

The fractions described above were obtained by crystallization from a 1 percent solution of UHMWPE in decalin. This solution was cooled slowly from 135 °C with rapid stirring until polymer appeared on the stirrer. This fraction was removed and the process was repeated until the next fraction appeared. Ten fractions were obtained by this method. About 12 percent of the material did not precipitate by the stirring process and was recovered as a residue when the solution was cooled. Limiting viscosity numbers ranged from 9 dl/g to 50 dl/g in decalin at 135 °C. Employing the conventional Mark Houwink relationship for lower molecular weight polymers this corresponds to a range of from about 900,000 to 10 million in molecular weight. The viscosity average molecular weight for the residue, if calculated in this way, is about 700,000 and would be expected to be very broad in distinction. This was confirmed in a preliminary GPC run which indicated the presence of material below 10,000, as well as some above 1 million.

Analysis of Ultracentrifugation Interference Patterns with Image Digitizer:  
Application to Molecular Weight Determination of SRM 1478 Polystyrene  
Subtask 5 of Task 12132

F. W. Wang and F. L. McCrackin

A new method for the analysis of ultracentrifugation interference patterns with the use of a commercial image digitizer is given. The application of the method to the sedimentation equilibrium data for SRM 1478 Polystyrene leads to a weight-average molecular weight of 37,400 g/mol having a sample standard deviation of 0.7 percent and expected systematic error limit of 2 percent.

Standards for Gas Transmission Measurements  
Subtask 6 of Task 12132

J. D. Barnes

Gas transport properties of polymeric materials are the major determinant of suitability for end use in a great variety of applications ranging from food and beverage packaging, industrial gas separation processes, and sterilization of medical devices, to substrates and packages for semiconductor products. Gas molecules are useful as probes of materials properties at the microstructural level. The measurement system for gas transport properties has suffered from a lack of reliable standards.

NBS is addressing these needs by developing improved measurement technology and by characterizing polymeric materials for use as Standard Reference Materials. The certification of SRM 1470 for its gas transmission properties with respect to helium, carbon dioxide, oxygen, and nitrogen has been completed. It is expected that this material will now be useful to a wider variety of users.



The recertification experiments produced approximately 720 values of the permeance and 540 values of the time-lag (the time-lag for helium was too short to measure). The results can be summarized in the form:

$$\hat{Q}(T) = \hat{Q}(23) \times \exp(\beta_Q [T - 23]) , \quad (1)$$

where the " $\hat{\phantom{x}}$ " denotes that the quantity is an estimated value as derived from fitting to the experimental data. "Q" represents either the permeance, P, or the time-lag,  $\tau$ , as appropriate and T is the temperature of measurement in °C. Values of  $\hat{Q}(23)$  and  $\beta_Q$  obtained from the analysis of the permeance and the time-lag data are given in tables 1 and 2 respectively. Since the time-lag for carbon dioxide depends upon the upstream pressure it is necessary to multiply the estimates obtained from equation 1 by a term of the form:

$$\exp[a_1 (p_u - 101.32) + a_2 (p_u - 101.32)^2] , \quad (2)$$

where the upstream pressure,  $p_u$ , is expressed in kPa. Estimates derived from equations (1) and (2) are valid only for pressures between 67.5 and 135 kPa and for temperatures between 18 and 31 °C, the ranges covered in our experiments.

Tables 1 and 2 provide additional statistical data that can be used to qualify the estimates derived from the fitting process.  $C_\mu$  is the coefficient of variation of the expected value, its numerical value largely determined by the sampling error arising from the selection of test specimens.  $C_s$ , the coefficient of variation of the "specimen effects," is a measure of the inhomogeneity of the lot of SRM material.  $C_r$ , the coefficient of variation of the residuals from the fit, is a measure of the extent to which individual data values depart from the model in equation (1). We have chosen not to construct the usual confidence or tolerance intervals because we do not have enough data on the distribution of the specimen effects. We are studying additional specimens to better define the structure and distribution of the specimen effects.

We are also seeking simple auxiliary measurements such as the specimen thickness or the density that can be used to define correction factors for reducing the measured values to a common basis. In the absence of such a scheme the specimen-to-specimen variability is the dominant factor limiting the precision that can be expected when comparing measurements among different stations in a measurement system.

The observed decrease of the time-lag for carbon dioxide with increasing pressure is consistent with published data that have been interpreted using a "partial immobilization" model. It is somewhat surprising that we do not observe a concomitant decrease in the permeance; perhaps the pressures used are too low or the pressure range is not broad enough.

The effects of partial immobilization are small in the range of conditions covered in our experiments. Users who wish to carry out measurements at much higher pressures and temperatures should realize that they may have to take explicit account of this phenomenon.



We are modifying our apparatus to operate at higher pressures and at temperatures encompassing the glass transition of poly(ethylene terephthalate) (PET) in order to better characterize the physics of partial immobilization and its relationship to the glass transition.

We are working to identify needs for materials with transmission rates that are both higher and lower than those of SRM 1470.

Since it is difficult to control processes for making plastic films in order to limit variability in their physical properties to one percent or less, we find that material inhomogeneity is an obstacle to the development of better SRMs. It is also difficult to use such materials as transfer standards because their characteristics often drift with time and test specimens often do not tolerate abuse suffered during the measuring process.

We have modified the software for our computer-controlled gas transmission measuring facility so that plotting of the raw data and reduction of the data to permeance and time-lag values are done on-line at the conclusion of each experiment. The software generates databases that can be input directly into statistical analysis programs over an NBS Net TIE.

New data acquisition hardware has allowed us to measure time-lags of less than one second. Further work must be done to detect the presence of instrumental time constants that can interfere with the measurement of the diffusion time-lags of the materials.

Table 1  
Fit Results for Permeance Data

Parameter	Gas				Units
	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	He	
P(23)	.0421	.352	1.722	13.79	pmol/m <sup>2</sup> ·s·Pa
β <sub>p</sub>	.0521	.0376	.0309	.0287	1/K
C <sub>μ</sub>	.023	.014	.018	.012	
C <sub>s</sub>	.057	.045	.056	.037	
C <sub>r</sub>	.050	.017	.010	.009	

Table 2  
Fit Results for Time-Lag Data

Parameter	Gas			Units
	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	
$\hat{\tau}(23)$	388.	1792.	2160.	sec.
$\beta_{\tau}$	-0.0597	-0.0763	-0.0624	1/K
$C_{\mu}$	0.013	0.022	0.014	
$C_s$	0.039	0.067	0.042	
$C_r$	0.024	0.094	0.016	
$a_1 \times 10^2$	--	--	-0.1873	1/kPa.
$a_2 \times 10^4$	--	--	0.0911	1/(kPa.) <sup>2</sup>

Diffusion of Polymers in Semidilute Solutions by Dynamic Light Scattering  
Subtask 7 of Task 12132

E. J. Amis, C. C. Han, and Y. Matsushita

The quasielastic light scattering from semidilute solutions of polystyrene in both good or theta solvent conditions has been measured as a function of molecular weight and concentration. We observe two distinct exponential decays separated by several orders of magnitude. The angular dependence of the decay constants is indicative of diffusive processes which we identify with the cooperative diffusion coefficient,  $D_c$  and the self-diffusion coefficient  $D_s$ . It is found that  $D_c$ , identified with the fast decay, increases with polystyrene concentration and is almost independent of molecular weight.  $D_s$  on the other hand decreases sharply with concentration and molecular weight. An explanation of the light scattering detection of these two diffusion coefficients can be made which is based only on assumptions inherent in the reptation model of diffusion in semidilute solutions. Over the range of molecular weight and concentration accessible to the technique the theta condition, measurements of  $D_s$  are in good agreement with scaling predictions of  $D_s \propto M^2 c^{-3}$ . For the good solvent measurements, the agreement with the prediction of  $D_s \propto M^2 c^{-1}$ <sup>75</sup> is only observed for a narrow window. The blob model gives some explanation for this behavior by allowing that even in a good solvent there is some distance below which excluded volume is unimportant. The chain is Gaussian and the chain shows theta-like ( $D_s \propto c^{-3}$ ) behavior. The blob model is however unable to account for the fact that for  $D_c$  the agreement with predictions is much better

in good solvent than in theta solvent. These experiments point out, once again, that the degree of agreement with scaling predictions is very much dependent on the concentration and molecular-weight ranges, the solvent quality, the property being examined, and the type of measurement.

Forced Rayleigh Scattering  
Subtask 8 of Task 12132

E. J. Amis and C. C. Han

So far this project has been limited to the construction of new instrumentation. In this technique a split laser beam is recombined at a small crossing angle on a sample which includes a trace of polymer labeled with a photochromic dye. This "writing" beam is pulsed to produce an interference pattern which bleaches a holographic grating in the sample. A second laser beam "reads" this pattern and is diffracted by the grating. As the labeled polymers diffuse in the sample, the grating is destroyed and thus, by measuring the intensity decay of the diffracted beam, the tracer diffusion coefficient of the labeled species can be obtained. Since the distance scale of this tracer method is very small (typically several orders of magnitude smaller than macroscopic tracer methods) it is possible to measure extremely small diffusion coefficients such as those expected for polymer molecules in concentrated solutions and melts. Recent theories of dynamics in concentrated solutions and melts should be tested by this experiment. Preliminary tests of the instrument have been very encouraging and with the installation of the detector electronics this instrument will be complete. Initial experiments will include measurement of free dye and small labeled polymers through dilute, semidilute, and concentrated solutions of various molecular weight polymers.

Concentration and Polydispersity Dependence of the Static Structure Factor  $S(q,c)$  and the Dynamic Characteristic Frequency,  $\Omega(q,c)$  in Dilute Polymer Solutions  
Subtask 9 of Task 12132

A. Z. Akcasu, B. Hammouda, T. P. Lodge, and C. C. Han

In all polymer characterization measurements, single chain properties such as the molecular weight and radius of gyration are obtained through extrapolation to zero concentration of measurements carried out at finite concentrations. It is clear that measurement precision can be greatly improved if single chain properties can be extracted directly from measurements carried out at finite concentrations and various polydispersities. It will be especially useful if scattering angle extrapolation can also be avoided in a scattering experiment. In this work, theoretical shape functions of static structure factor as a function of the scattering vector,  $q$ , and concentration,  $c$ , are developed and tested through light and neutron scattering data. Also, calculations of the dynamic characteristic frequency  $\Omega(q,c)$  and decay rates are performed for polydispersed systems and compared to dynamic light-scattering data at the  $\theta$  temperature.



Single Chain Conformation in Phase Separated Diblock Copolymer Systems  
Subtask 10 of Task 12132

H. Hasegawa, E. J. Amis, T. P. Lodge, and C. C. Han

Polymer properties can be greatly altered by controlling the size and shape of the phase separated domains of polymer blends or copolymer systems. It is obvious that the single chain statistics in these phase separated domains play an important role in the understanding of the equilibrium and nonequilibrium properties of these systems. In collaboration with Dr. H. Hasegawa and the Kyoto University group, we have prepared well controlled model systems of polystyrene-polyisoprene which have regular lamella domains. Dimensions of deuterium labeled polystyrene block of this diblock copolymer and also dispersed homopolystyrene molecules were measured at different directions relative to the domain orientations by small-angle neutron scattering (SANS).

Small Angle Neutron Scattering From Block Copolymers of h-styrene and d-styrene  
Subtask 11 of Task 12132

T. P. Lodge, Y. Matsushita, E. J. Amis, and C. C. Han

In our effort to investigate the temperature and molecular weight dependence of polymer dimensions, various experiments and theoretical models have been investigated. It is true that the chain end effects are normally neglected in both mean field and modern scaling theories. Although perturbation theory attempts to differentiate the excluded volume effect as a function along the chain contour, it is not expected to work well in the good solvent limit. In this work, we performed SANS measurements of labeled chain segments located at various positions along the chain contour. As far as we know, this is the first time the importance (or unimportance) of neglecting the chain end effect has been tested experimentally through direct measurements of a set of well prepared and well characterized polymer samples.

Static Light Scattering  
Subtask 12 of Task 12132

C. C. Han, H. L. Wagner, and D. B. Minor

The light scattering photometer has been redesigned and fabrication has been completed. Preliminary measurements show that the problem of thermal instability has been overcome because of a new highly stable rotory table and isolation of the high temperature bath from the optical train. Other features which have been incorporated are a stepping motor drive for the rotory table, and a 4 MW He-Ne laser rather than the 2 MW one used previously.

P. H. Verdier and D. E. Kranbuehl

The dynamic behavior of polymer chains is important to improving both characterization and processability of polymers. The principal methods used to estimate molecular weight, and in particular gel permeating chromatography, the only method available at present for estimating distribution in molecular weight, are dynamical, nonequilibrium experiments which depend in part upon the relaxation of polymer chains in dilute solution. In its present state, the theory of these systems does not allow the calculation of molecular weight directly from measured quantities; a series of calibrants of known molecular weight is required. Improvements in the theory could reduce or even remove the need for calibrants, allowing the determination of molecular weight distribution of polymers for which calibrants are not available.

The processability and the final characteristics of both plastics and elastomers depend in large part upon the relaxation behavior of the high-polymer chains of which these materials are primarily composed. More realistic theoretical treatments of polymer melts and elastomers, which must start with more realistic treatment of the dynamical behavior of the individual chains, will lead to more efficient processing and better fabricated end products. A major shortcoming of the present theory is its inability to treat chain entanglements in a realistic way. Our present work is aimed primarily at the study of entanglement effects, using a combination of analytical and computer simulation techniques. The simulation results provide data on simple model systems and serve to guide the development of better theoretical treatments.

Work in this area is proceeding along two main lines. First, there is at present an unresolved disagreement in the literature regarding the interpretation of the time-correlation functions obtained for flexible chain molecules in the quasielastic light scattering experiment. It is not clear whether these functions exhibit the entire spectrum of chain relaxation times or are dominated by the longest relaxation time. By a combination of analytical and simulation techniques, we have shown that very slight changes in the local chain-movement rules can change the behavior of the resulting time-correlation functions from one extreme to the other, suggesting that the existing disagreement is due at least in part to the use of insufficiently detailed chain models. These results will be published during the coming year. Second, as a step in the direction of investigation melt properties, we are carrying out simulation studies of systems of many interacting chains, with chain densities corresponding to concentrated solutions and melts. Interpretation of the results of these studies is underway, and will continue in the coming year.



Monte Carlo Calculations of the Hydrodynamic Radii of Polymers  
Subtask 14 of Task 12132

F. L. McCrackin

The values of the hydrodynamic radii of chains at infinite dilution on a cubic lattice were computed. The chains were created by a Monte Carlo simulation in which both volume exclusion and energetics of nearest neighbor interactions were taken into account. Other quantities, such as radii of gyration, were also computed for the chains. The ratio  $\rho$ , the radius of gyration to the hydrodynamic radius of the chains at the theta point, were compared to experimental values obtained from quasielastic light scattering and elastic light and neutron scattering. Reasonable agreement was obtained; in fact, the experimental values of  $\rho$  showed better agreement with the Monte Carlo calculation than with the analytical Gaussian coil model.

The calculations were also performed for various values of the energy parameter, corresponding to good solvents. The computed values of the hydrodynamic radius are found to be in reasonable agreement with published data of the variation hydrodynamic radius of polystyrene with temperature. The results are also in agreement with calculations of A. Z. Akcasu based on the blob model of polymer solutions.

The calculations are being performed for two interacting chains. The results will be interpreted as the properties of polymers in dilute solutions. The variation of radii of gyration and hydrodynamic radii with concentration and the second virial coefficient will be calculated and compared with experiment.

Span of an Adsorbed Random Flight Chain Calculated on the Basis of the deGennes Model  
Subtask 15 of Task 12132

R. J. Rubin

P. deGennes showed that the one-dimensional step density distribution of monomers in his model (normalized to  $N$ , the number of monomers) is

$$n(x) = 2kN e^{-2kx}, \text{ for } k > 0, \quad (3)$$

where  $x$  is the distance from the solution surface, and the boundary condition of the random flight propagator at the solution surface is

$$1/G \partial G / \partial x \big|_{x=0} = -k.$$

G. Weiss and I have derived the probability density of the span of an adsorbed polymer chain in deGenne's model. The average value of the span is

$$\langle X \rangle = (2k)^{-1} \ln N \text{ for } N \gg 1.$$

This quantity is identically equal to the distance from the adsorbing solution surface at which the exponential step density given in Eq. (3) is equal to unity, i.e., if the equation



$$2kNe^{-2kx} = 1$$

is solved for  $x_1$ , then  $x_1 = \langle x \rangle$ . A paper outlining this calculation of the probability density of the span has been prepared and submitted for review.

Validation of the "Weak Adsorption" Diffusion Equation Plus Boundary Condition Model of deGennes  
Subtask 16 of Task 12132

R. J. Rubin

We have solved the discrete lattice random walk model for a polymer chain near a surface when there is an absorbing layer at  $K = -1$  and each segment of a chain configuration in layers  $K = 0$  to  $\ell$  results in a Boltzmann weighting factor  $e^{\varepsilon/kT}$  multiplying the probability of that configuration. [ $\varepsilon$  is the energy gained when any chain segment occupies any one of these  $\ell + 1$  layers. Thus, the weighting factor of a chain configuration in which  $m$  segments lie in layers  $k = 0$  to  $\ell$  is  $e^{m\varepsilon/kT}$ .] We have solved the analogous diffusion equation model for this problem [this diffusion equation was first proposed by J. Pouchly', Coll. Czech. Chem. Comm. 28: 1804; 1963]. The deGennes model may be regarded as a limit of the Pouchly' model which in turn is the continuous analog of the discrete model described above. A paper comparing polymer chain behavior in these models is in preparation.

A New Equation of State Model for Polymers  
Subtask 17 of Task 12132

I. C. Sanchez

A new statistical mechanical model for a chain liquid has been developed which shows solid-liquid transition as well as a liquid-vapor transition. This new model is a generalization of the lattice fluid model developed by Sanchez and Lacombe. The basic idea is that the mers of a  $r$ -mer can exist in either of two states: ordered or disordered. In order for an  $r$ -mer to crystallize it must be in a particular orientation. For example, in an alkane the monomers must all be in a trans configuration to crystallize. Or if the mers have a permanent dipole, they would all have to be oriented correctly to crystallize.

We are exploring several different applications for this model. First it may prove to be an excellent model for describing glassy behavior in polymers. It should also be a good model for describing polar polymer mixtures that strongly interact. Finally, it may prove to be a relatively simple model that will be able to semiquantitatively describe the PVT properties of water.

## ASTM Activities

### Subtask 18 of Task 12132

J. D. Barnes

J. D. Barnes serves as Chairman of ASTM Subcommittee F-2.93 and D-20.13. These subcommittees provide assistance in matters relating to the design of experiments for evaluating the precision of test methods for the parent ASTM Committees. This assistance takes the form of approval of round-robin protocols, critique of precision statements, and statistical education for task group leaders. Recent round-robin activities have included a test method for Bond Strength within Committee F-2 and a study of the density gradient technique (ASTM D-1505) for Committee D-20. Dr. Barnes has served as a consultant to task groups working on Rockwell hardness of plastics, tensile properties of film and sheeting, and thickness measurements using a magnetic sensor.

Dr. Barnes has recently been appointed Chairman of Subcommittee D-20.70's section on gas transmission measurements.

Dr. Barnes organized a symposium on Fourier transform infrared (FTIR) methods in plastics characterization and processing that attracted five invited papers that were heard by about 75 participants at an ASTM meeting in Williamsburg, VA.

## Rubber and Rubber Compounding Standard Reference Materials

### Subtask 19 of Task 12132

G. B. McKenna and G. W. Bullman

NBS provides rubber and rubber compounding Standard Reference Materials that are used by the rubber industry for quality control in production of rubber and its processing into articles. During the past year recertification of SRMs 371 (Sulfur) and 372 (Stearic Acid) have been completed. These compounding materials are referenced in ASTM standards and used to ensure the processibility of rubber materials. The Mooney viscosity standard, SRM 388, butyl rubber, has also been renewed during the past year. This standard is widely used by the rubber industry for calibration of Mooney Viscometers which are increasingly used for on-line quality control during the production of synthetic rubbers.

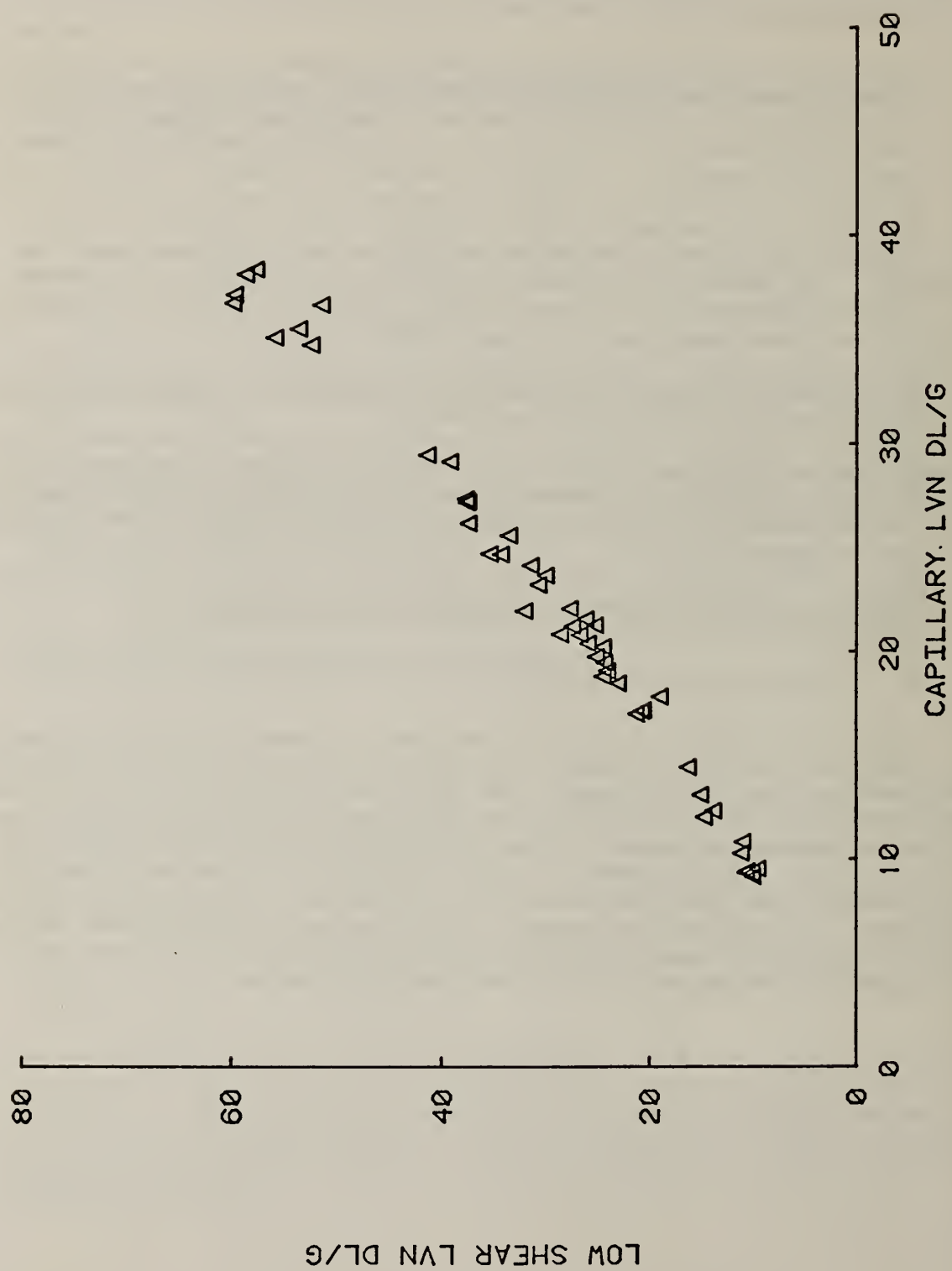


Figure 1 Relation between LVN at zero shear and LVN measured in a Capillary Viscometer.



## TESTS, STANDARDS AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS

### Task 12135

The objective of this research is to provide test methods and standards to sectors of the health care industry that make critical use of materials. Materials research and techniques are pursued with the goal of developing dental adhesive composite restorative materials of greater durability and wear resistance, improved base metal alloy alternatives to the costly gold alloy dental prostheses, and test methodology applicable to porcelain/alloy combinations. Knowledge of the structure and physical chemistry of biologically important calcium phosphates is used to develop improved preventive dental techniques. Improved test methodology is sought for characterization of the surfaces of surgical implant materials for defining the interactions that occur thereon. Means for characterizing the porosity of low modulus, polymeric, medical implant materials are being investigated.

Dental research directions in support of the objective are established collaboratively with the American Dental Association, the National Institute of Dental Research, and the Department of Defense Medical R&D Command. Medical materials research is guided by close interaction with the Bureau of Medical Devices, Food and Drug Administration, and the ASTM F-4 Committee (Medical and Surgical Materials and Devices.)

### Dental Composite Chemistry and Development

#### Subtask 1 of Task 12135

G. M. Brauer, J. M. Antonucci, J. W. Stansbury, J. M. Cassel, S. Ventz<sup>1</sup>, and R. L. Bowen<sup>2</sup>

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<sup>2</sup>Research Associate, American Dental Association

With the view that reducing polymerization shrinkage and residual unsaturation in dental resin systems would make them more useful in efforts to achieve adhesive bonding, better color stability, and improved durability in composite restorative systems, we have continued to investigate new comonomer combinations whose structures would suggest their applicability for this purpose. A particularly promising monomer is the high molecular weight, moderately viscous polythiol pentaerythritol tetra (3-mercaptopropionate) (PETMP). It has potential not only as a useful comonomer but also as a polymerization accelerator. With multifunctional methacrylates that readily undergo free radical self-addition reactions of vinyl groups to create a propagating polymeric chain, the use of polythiols leads to a hybrid polymer composed of polymethacrylate and polythioether elements in the network structure. Preliminary results using infrared spectroscopy indicate there is a significant reduction in vinyl unsaturation when modest concentrations (< 5 percent by weight) of PETMP are employed in a typical dental resin formulation. Levels of PETMP between 1 and 5 percent have produced composite materials with excellent esthetics and color stability. The improvement in color stability and esthetics in many of the resin systems examined may be due

to the fact that use of PETMP allows a reduction in the concentration of amine accelerator, a recognized source of color problems with composite restorations. A further important potential advantage to be explored with PETMP is that it appears to enhance the storage stability in the dissolved state of such highly biocompatible polymerization promoters as ascorbic acid.

We have found the bulky monomethacrylate, isobornyl methacrylate (IBM) can be used to dilute 2,2-bis[P-(2-hydroxy-3-methacryloxy-propoxy)phenylene]-propane (BIS-GMA) and composites with good setting characteristics, color and mechanical properties are obtained. Unlike many long chain alkyl methacrylates that have sluggish ambient temperature rates of polymerization, IBM is more reactive even than methyl methacrylate. Homopolymers of IBM in contrast to other alkyl methacrylates have a slightly higher glass transition temperature ( $T_g$ ) than that for poly(methyl methacrylate) (PMMA) and this may prove advantageous in developing greater durability in composite restorations. However, when used as a comonomer with a hydrophobic, highly fluorinated polymethacrylate for purposes of reducing water sorption, the IBM appears to yield only marginal strength composites.

Our previous investigation of the silanization treatment of composite filler particles had shown that incorporating certain n-alkyl amines and selecting a hydrocarbon carrier for 3-methacryloxypropyltrimethoxysilane increased the reinforcing capability of the filler particles. This beneficial effect has now been shown to be optimized using a 2 percent solution of n-propyl amine and 0.5 percent of silanizing agent in cyclohexane. Initial tensile strengths of composites is improved significantly and the rate of water-induced loss of strength as determined for two and six months at 37 °C is reduced.

#### Improved Bonding Techniques and New Dental Cements Subtask 2 of Task 12135

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While effective bonding to tooth enamel is presently achieved by means of acid etch treatments, similar treatments of dentin have not shown satisfactory results. We are currently investigating several potential means of resolving this problem.

Alkylcyanoacrylates polymerize rapidly at room temperature and certain ones have been previously shown to yield a very strong initial bond with dentin that unfortunately is weakened significantly on exposure to water. To address this shortcoming we have begun an effort to prepare a cyanoacrylate with cross-linking capability, i.e., allyl 2-cyanoacrylate. The synthesis involved esterification of cyanoacetic acid to allyl cyanoacetate which was then reacted with paraformaldehyde to give poly(allyl 2-cyanoacrylate). While we have made repeated efforts to depolymerize



this polymer to yield the desired monomer, we have not been successful to date and currently we are examining alternative means for its preparation.

A new bonding procedure that uses an acid mordanting solution, a surface active monomer, and a coupling agent to prepare dentin and enamel for bonding to composite resins appears to have much promise. An aqueous solution of ferric oxalate is applied, washed with water, and blown dry. An acetone solution of the surface active comonomer NTG-GMA, the adduct of N(p-tolyl)glycine and glycidyl methacrylate is applied, followed by pure acetone and drying with air. An acetone solution of the addition reaction product of pyromellitic dianhydride and 2-hydroxyethylmethacrylate is then applied and the surface blown dry before pressing a composite resin formulation against the surface and allowing it to harden (polymerize). Scanning electron microscopy results show that the iron oxalate solution alters the tooth surface layers. The coupling agents then provide molecules which are bound to the modified surface and can polymerize with the resin of the composite material applied subsequently. Bond strength measurements confirm that the strong bonding initially achieved is retained on exposure to water for up to five days. A real possibility exists for improving treatment of erosion, root caries, and other conditions by reducing the amount of dentin that must be cut for mechanical retention.

Dental cements with good biocompatibility, improved mechanical properties and resistance to disintegration on exposure to the oral environment are needed. Zinc oxide-eugenol dental cements, while possessing many desirable properties, are relatively soluble in oral fluids and adhere poorly to acrylic restorations, bone, or dental tissues. Furthermore, because of the electron-rich phenolic hydroxyl group in eugenol, these cements inhibit free radical polymerization and hence hardening in any dental resin or composite system subsequently placed in contact. Previous research to develop substitutes for the eugenol component has not produced cements with adequate physical properties. Recently, however, we have developed a non-eugenol based cement that combines zinc oxide, ethoxybenzoic acid (EBA) and esters of vanillic acid. It has been demonstrated to have not only desired physical properties but certain important chemical properties. These cements do not inhibit free radical polymerization, and adhere strongly, even in water, to nonprecious metals, amalgams and composites. They do not disintegrate in water and considerably exceed the requirements of the ANSI/ADA Specification No. 30. Thus, a portion of the cement, when used as a temporary filling, can be retained as a base for acrylic resin restorations. The material, with suitable modifications, looks most promising as a base, temporary restorative, and endodontic cement. Cementitious restoratives with drastically improved mechanical properties which could find applications as long-lasting temporary fillings were prepared by incorporating a dimethacrylate monomer, peroxide initiator, amine accelerator, and glass reinforcing fillers into the cement formulations. We have prepared (by synthesis) sufficient quantities of a promising vanillate, a hexyl vanillate, to allow biocompatibility testing. Samples of the powder and liquid have been sent to six institutions for biological evaluation of the basic formulation.



To increase the strength of these cements beyond the already respectable levels achieved so that increased dental application can be made, we have investigated cements prepared with ZnO, Al<sub>2</sub>O<sub>3</sub>, hydrogenated rosin and silanized glass (coated with benzoyl peroxide) as the powder and hexyl vanillate, decamethylene dimethacrylate, a fast acting amine accelerator and a stabilizer as the liquid. Cured cements with good working properties and strengths, four to seven times that obtainable with zinc oxide-eugenol formulations, were obtained. These vanillate-based cement modifications offer promise as intermediate restorative materials.

#### Wear Mechanisms, Wear Testing and Improving Durability in Dental Composite Materials

##### Subtask 3 of Task 12135

W. Wu, J. E. McKinney, E. E. Toth, and J. M. Cassel

Development of improved dental restoratives requires proper evaluation criteria to predict the long term in vivo performance of these materials. Microdefect analyses involving a photographic silver staining procedure and a small angle x-ray scattering (SAXS) technique have been applied to quantify the extent of subsurface damage in both in vivo and in vitro worn composite materials. Since we find that there is subsurface damage beneath the nonstress bearing as well as the stress bearing surfaces in clinically worn restorations, we have theorized that the oral environment plays an important role in the deterioration process. Consequently, the diffusion of food simulating chemical solvents into dental composites and the influence of this diffusion in softening the polymeric matrix as a prime step toward loss of material has been investigated.

Initial measurements of diffusion coefficients for water in typical composites, using a quartz spring mass sorption technique, indicated that the diffusion rates were Fickian and that both diffusion rate and water sorption were significantly reduced in composites cured at 60 vs 37 °C. By infrared measurement of residual double bond concentration in the dental resin as a function of the curing time and correlation of these results with differential scanning calorimetry measurements of the curing that occurs as the temperature is raised from the initial 37 °C, we have shown that the more delayed the temperature rise is, the less is the effect on curing. This would dictate that if increased curing by heating were to be made clinically viable, it would need to be accomplished almost immediately following placement of the restoration.

Measurements of Knoop hardness on a conventional, a strontium glass filled, and a visible light activated composite after each was cured at 37 °C and subjected to immersion in food simulating solvents for one week demonstrated that each was softened to the greatest extent by 75 percent ethanol/water concentrations. The largest effects at this ethanol concentration were observed with the conventional composite and the least with the light activated material. Immediately following completion of the immersion in the food simulating solvents, wear measurements were made using pin on disc wear equipment. While the wear analysis is not completed, the wear for both the conventional and the light activated composites when plotted against the solubility parameter of the food

simulating medium follow the same trend, e.g., maximum wear rates at 75 percent ethanol concentration, as observed with the Knoop hardness measurements. When the in vitro wear rates of composites cured at 25 and 60 °C and then immersed in 75 percent ethanol in water media were compared, the wear rates of the composites cured at the higher temperature were one-fourth that of the lower temperature-cured material. These results are in perfect accord with the preliminary diffusion data referred to earlier and support our contention that ways (heat or otherwise) must be found to significantly increase the degree of polymerization in the composite resin during the restoration process.

#### Composite Restorative Materials

##### Subtask 4 of Task 12135

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Restorative dentistry is that form of dental practice that utilizes the most time of the Army dentist as well as the soldier dental patient. Composite materials are prime components in restoration procedures. Greater durability and satisfaction would be achieved with such materials if the marginal adaptation (resistance to microleakage) were improved. For the Army it is also important to improve the storage stability of such materials and earlier efforts in this project have defined the prime sources of storage instability and practical means for optimizing storage stability with presently available materials.

This year we have demonstrated the improved sensitivity in microleakage measurement that can be achieved by using a silver staining technique as an alternative to a more cumbersome radiotracer x-ray film procedures. Microleakage determinations have been made on a series of experimental composites formulated to be hydrophobic rather than mildly hydrophilic as are current commercial dental composite materials. While a dual silanization procedure for fluorinating as well as silanizing glass filler particles did not reduce water sorption in the composite, the increased compatibility of such glass with fluorinated monomers may offer a means of achieving higher filler loadings and hence improved physical properties if needed. Combining a commercially available fluorinated diluent comonomer, pentadecafluorooctyl methacrylate, with two commercially available nonhydroxylated analogs of BIS-GMA, the basic resin in conventional dental composites, resulted in a composite with adequate physical properties but did not enable us to reduce water sorption significantly.

Since we hypothesize that to significantly lower both microleakage and water sorption we need a resin system that is hydrophobic and that on curing shrinks minimally, we have begun examination of composite formulations derived with the very large experimental prepolymer, PFMA, a highly fluorinated polymeric (approximately 10 repeating units) comonomer with multiple methacrylate groups for chain extension and cross-linking. To achieve workable viscosities we are diluting with highly hydrophobic



comonomers such as 1,10-decamethylene dimethacrylate or neopentyl glycol dimethacrylate. Results to date indicate promise in terms of reduced water sorption and microleakage and respectable physical properties.

Porcelain Fused To Base Metal Alloys and Dental Ceramics  
Subtask 5 of Task 12135

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A major cause of failure in porcelain-fused-to-metal restorations involves cracking or delaminating of the porcelain veneer. Apropos to this situation we developed a new concept for evaluation of porcelain-to-metal bond strength. The test uses four-point bending of a metal strip to which porcelain squares have been fused and measures tensile strengths of porcelain-to-metal bonds (without influence from shear stresses). Recent finite element model (FEM) calculations confirm that simple beam theory provides an adequate description of the stress within the system. The effective stress is virtually the same as the normal tensile stress (i.e., other stresses, such as shear stresses are small) and both are essentially the same (to within about 6 percent on the average) as stresses calculated by beam theory. Moreover, a smooth transition of stress from metal through porcelain is indicated by FEM calculations which were conducted using an elastic modulus for metal,  $E_m$ , twice that for porcelain,  $E_p$ , i.e.,  $E_m/E_p = 2$ .

Preliminary test results have shown that two to four strength determinations can be made from one test specimen. Application of St. Venant's principle resulted in specimen test design intended to leave such successive strength determination independent of previous fractures. What is determined is either the porcelain-to-metal bond strength or the porcelain fracture strength. Test results show that for strong porcelain-to-metal bonds only porcelain fractures are recorded. For weak bonds at interfaces only interface fractures are recorded. In other cases, mixed failures occur, i.e., a porcelain-to-metal bond failure may be preceded by a porcelain fracture and followed by two more porcelain fractures; other possibilities are obvious. Because the order of failures (fractures) is expected to be toward continuously increasing strength values, statistical interpretation in terms of ordered statistics will be investigated. Experiments are currently in progress to develop meaningful statistical data as the preliminary testing has been essentially completed.

Industry has expressed great interest in the new test methodology as it offers the potential of producing quantitative as well as qualitative information on porcelain-to-metal bonding and on relatively easily prepared specimens which yield several pieces of information per test



run. Three dental companies committed R&D personnel to work as visitors for one week in an evaluation of the test methodology.

We have previously developed rationale for utilizing the change in gap of a porcelain veneered split metal ring as a measure of porcelain/alloy stress compatibility. Recent work has centered on development of the FEM which incorporates the viscoelastic properties of porcelain. Difficulties have been experienced with the continuity of the computer program and these are currently being worked on. This, coupled with a recent concentration of effort on the porcelain-fused-to-metal bond, testing and castability evaluations has resulted in delaying progress. This work is expected to renew in intensity as we are joined by guest workers from Germany and Japan.

The thermal expansion behavior of many experimental porcelain compositions have been determined. These porcelains have been formulated to achieve very low fusing temperatures, i.e., below 800 °C. The coefficient of thermal expansion usually varies with temperature and, in general, the relationships can be grouped into three different classes: (1) a monotonic increase with temperature; (2) an irregular change with temperature; and (3) no change with temperature. These findings demonstrate that matching the coefficients of thermal expansion of metal and porcelain at only one high temperature as is usually done may not lead to an optimal porcelain-to-metal system.

Mathematical analysis has been performed on the data obtained in studies of the effects of various ingredients that influence the fusion temperature in experimental porcelains. It was found that a wide range of  $B_2O_3$  concentrations has a surprisingly small effect on the fusion temperature of these experimental porcelains.

During the past year new investments for use with titanium metal have been investigated. The preliminary studies showed that  $SiO_2$ ,  $Al_2O_3$  and  $AlPO_4$  are ingredients to be avoided. Molten titanium acts as an extremely strong reducing agent and reduces  $SiO_2$  while forming a titanium oxide. It was found that similar reactions occur with aluminum oxide and aluminum phosphate. Three oxides that are relatively stable have been identified, namely those of magnesium, yttrium and zirconium. However, moldcoats of these oxides, used as liners with conventional phosphate-bonded investments, were unsuccessful because of poor adherence to the investment.

#### Dental Casting Alloys and Investments Subtask 6 of Task 12135

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<sup>2</sup>Research Associate, U. S. Navy

Dental casting alloys based on gold or cobalt have, in recent years, faced serious problems of cost and availability. Though these problems have eased somewhat, they could recur at any time. The use of nickel alloys as substitutes has faced some concern for their toxicity and induced allergic responses in certain patients. Titanium-based alloys

would seem to offer a satisfactory alternative, being strong, corrosion-resistant, relatively inexpensive, widely available, and nontoxic. A study of the effects of interstitial solutes (O, N, C) on phase equilibria in Ti-rich Ti-Al alloys was initiated. Also, high-temperature neutron diffraction experiments are planned in collaboration with the NBS reactor group. Equipment designed to permit observations of alloys to 1200 °C is under construction.

With the introduction of numerous dental alloys as alternatives to gold alloys, it becomes increasingly important to develop a castability test that is indicative of an alloy's ability to fill a mold of specific design under a set of prescribed conditions. Such a test has been under development in this laboratory and in its present stage assesses the percentage,  $C_v$ , of cast segments of a polyester grid pattern, figure 1.

We have applied the test to a number of dental alloys using the manufacturer's recommended mold and alloy casting temperatures. Results of  $C_v$  determinations are shown for several dental alloys as they are cast using different investments, figure 2.

The following observations support the validity of applying the test method: (1) some of the presently employed alternative alloys compare favorably in castability to those of high noble content; (2) the brand of mold investment used can produce a significant effect on the castability of some alloys; (3) as expected, the castability value increases as mold and casting temperatures increase; (4) an optimal mold and casting temperature can be discerned for each alloy beyond which castability values show little change; (5) for each alloy a different amount of heat above liquidus ("superheat") is required to produce the optimal casting temperature; (6) the effect of mold temperature on castability may be greater than previously thought for some alloys and less significant for others; and (7) as the limiting value for castability is approached ( $C_v = 100$  percent) the standard deviation (SD) from the mean determination of  $C_v$  appears to decrease. Hence, larger SDs for some alloys may well be indicative of potential for further optimization of conditions for casting of that alloy.

As can be seen from the foregoing observations, the investment, the temperatures used, and probably many other factors have to be taken into account when comparing the castability of dental alloys. As a further example of this, preliminary studies using torch casting indicate that the castability value for some alloys is altered significantly from those cast by induction melting. A question that naturally arises is: what threshold castability value is acceptable? This again brings up the point previously made, that the test method should be used where relative comparisons are desired and that the significance of the absolute castability value of any alloy system by itself is an unanswered question and is at present a matter of conjecture.

It is apparent from the data that the standard deviation of the castability value,  $SD_{C_v}$ , is a function of  $C_v$ , the casting temperature,  $T_c$ , and mold temperature,  $T_m$ , i.e.,  $SD_{C_v} = f(C_v, T_c, T_m)$ . The form of the relationship



has not yet been determined (standard statistical transformations have been found not to apply and are the subject of continuing work). We only wish to note at this point that if a universally applicable relationship can be found it will significantly reduce the number of experiments required to completely determine castability for any alloy as a function of temperature. The benefits of such a relationship should be obvious to those engaged in quality control, product development or setting of standards.

A final point should be made on the repeatability of the results as reported here. One base metal alloy having a castability value toward the center of the range was cast on five separate occasions to monitor this aspect. The results were statistically indistinguishable.

#### Dental Chemistry and Preventive Dental Treatments Subtask 7 of Task 12135

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The objective of this project is to develop and apply fundamental information on the solubilities and crystallographic structures of biologically important calcium-containing phosphate compounds to the development of improved dental caries preventive techniques. Important portions of this effort are concerned with (1) development of physico-chemical models of the caries process to include insight into the mechanisms by which impurities and defects are incorporated onto tooth enamel, and (2) application of solubility phase diagram analysis and kinetic data to the development of more effective enamel acid-etch bonding treatments and improved topical fluoride procedures.

During the past year, the crystal structures of  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  and  $\text{Ca}(\text{NH}_4)\text{PO}_4 \cdot 7\text{H}_2\text{O}$  were determined. Structure analysis of a calcium phosphate-urea complex, predicted to possess a layer-type structure, has revealed it to be a non-layer type compound. A structural study of natural and synthetic crystals of bobierrite,  $\text{Mg}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  revealed the positions of the hydrogen ions in this member of an important and varied class of compounds. Research on the structure of octacalcium phosphate,  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ , and its role in biomineralization continues to be a major activity. During the report period, the refinement of the crystal structure was completed; important evidence for its participation in the formation of enamel mineral was gained. A chemical procedure was developed that for the first time makes it possible to measure separately the rate of its formation and rate of its conversion to the basic mineral of bone and tooth.

The work on caries mechanisms is carried out on three levels: (1) theoretical considerations to develop physicochemical principles which might govern the caries process; (2) bench-scale experiments to validate such principles; and (3) ultramicro studies on tooth sections to establish on a quantitative basis the events occurring within the tooth itself.



Theoretical considerations focus on the idea, heretofore largely ignored, that the relative rates of diffusion of ions into and out of the lesion are important parameters in the caries process. It was predicted and subsequently confirmed that factors such as the presence of fluoride, the membrane-like behavior of the outer surface of the tooth and the plaque, and neutral salts normally present in the saliva are among the important parameters affecting the rate of the caries process. Bench-scale studies showed that the rate of demineralization was increased by a factor of 80 when the membrane transmitted positive ions selectively as compared to when it transmitted negative ions selectively. Also,  $F^-$  greatly reduced the rate of demineralization (this effect appeared to be greatest at pHs below about four). These results provide further evidence in support of a cariostatic mechanism for  $F^-$  developed at NBS and suggest that the caries resistance of teeth may be increased by modifying the selectivity of the tooth surface to transmission of ions. In ultramicro studies, good progress was made in developing pieces of equipment and procedures for working in the nanoliter ( $10^{-9}$  liter) sample range. The techniques have been extended to include analysis of plaque samples where the volumes of plaque are sufficiently small so that they can be collected from a single tooth.

In addition to the studies on the role of fluoride in the caries mechanism, work continues on the new topical fluoridation procedures developed in these laboratories. These procedures are based on the idea that tooth mineral (primarily  $Ca_5(PO_4)_3OH$ ) reacts very slowly with  $F^-$ . However, as a part of the fluoridation treatment, some of the  $Ca_5(PO_4)_3OH$  can be converted to another compound,  $CaHPO_4 \cdot 2H_2O$ , which reacts rapidly with  $F^-$ . Through the use of procedures based on this principle, it has been found possible to greatly increase the permanently-held  $F^-$  content of teeth. The clinical relevance of this increased  $F^-$  content remains to be established, but it is plausible that it should be beneficial.

A successful remineralization procedure would drastically alter the procedures used to treat incipient lesions. During this period, initial steps were taken to develop procedures for testing remineralization formulations based on prior basic studies carried out in these laboratories. The initial results are encouraging. Substantial progress was made in developing techniques to remineralize exposed and sensitive root surfaces. A procedure was developed which by laboratory criteria appears to be a successful remineralization procedure. It is expected that preliminary clinical evaluations will be carried out in the near future.

#### Clinical & Laboratory Investigation of Dental Amalgams, Composites & Cements

##### Subtask 8 of Task 12135

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Dental restorations vary considerably with time. Among the factors influencing the success or failure are: (1) the material and how it was handled by the operator; (2) the cavity preparation; and (3) the patient's

home care. Sorting out the factors contributing to the durability of a restoration requires a careful combination of clinical studies and laboratory analyses.

Observations of amalgam restorations placed 7 to 8 years ago are continuing in the clinic and laboratory. Amalgams that are high in copper content and are highly creep-resistant continue to be superior. The relation between marginal integrity and creep, if the creep is below 2 percent, is more dependent on operator manipulation than on creep; for example, creep values of 0.2 or 0.8 percent do not seem to correlate with the quality of the margins. Alloy composition and the resultant amalgam composition influence the aging characteristics. Laboratory measurements of dimensional change have been made for six years on specimens stored at 23, 37, and 60 °C on either unrestricted specimens or in specimens restricted by placement in simulated Class V Cavities in steel blocks. Zinc, tin, and mercury contents, each independently, affect the dimensional changes: increasing the zinc and mercury contents seems to cause an expansion, while tin over 28 percent usually results in shrinkage. There are, however, some exceptions. As we gain a better understanding of the rheology and the internal phase changes, it should be possible to extend the useful life of amalgam restorations.

One of the principal defects in composite restorations continues to be imperfect sealing of gingival margins. Laboratory studies confirmed that microstructural bonding of composites to enamel successfully prevents microleakage, and that the paucity of enamel at the gingival margin obviates sealing through the use of acid-etch bonding. Currently the only commercially available materials that are adhesive to dentin are those with carboxyl groups. Clinical observations were made with glass ionomer cements which contain these groups, and the adhesion does appear to be good; the visual opacity of these materials continues to be a problem.

There is also an available product that utilizes a coupling agent that is polymeric and contains carboxyl groups. This system does not call for treatment of the dentin with citric acid (which opens the tubules to irritants). In vitro and in vivo testing of this coupling agent-composite system is being pursued to assure that this combination can be advocated for general use. If so, this will reduce staining and decay at the gingival margins of composite restorations.

#### Adhesion of Synthetic Polymers on Solid Surfaces Subtask 9 of Task 12135

R. E. Dehl and W. H. Grant

The adhesion of polymeric protective coatings, with its many important commercial applications, is hampered by a lack of fundamental understanding of the interaction of polymer molecules with solid surfaces. It is the energy of adsorption of individual polymers with a surface which determines the adhesive strength of an adhering polymer film, and there is a need for more specific information about such factors as the role of individual polymer segments attached in governing the adhesive strength. One measure of the energy of attachment is the rate at which polymers desorb



from solid substrates when the coated surface is placed in contact with a suitable solvent. The results of previous NBS studies, using radiolabeled polystyrene to detect the amount of polymer remaining on the surface, indicate that the rate of desorption decreases with increasing molecular weight of the polymer and with the amount of polymer initially adsorbed. We have also previously reported that the rate of desorption of tritium-labeled polystyrene from solid surfaces depends not only upon the amount adsorbed, but also upon the way in which a given level of adsorbance is achieved. Such factors as the time of adsorption, which can be controlled by adjusting solution concentration, and preadsorption to higher adsorbance levels were found to affect the desorption rate from the same adsorbance level. A model was proposed to explain these phenomena, based upon two or more types of adsorption sites having different energies of attraction for polymer molecules.

During the past year, we have found that the rate of adsorption and desorption studied over long periods of time may be complicated by the tendency of high molecular weight (MW) species to degrade in time. One polystyrene solution which had been used for several months was found by gel permeation chromatography (GPC) to have a broader MW distribution and a lower average MW than a fresh solution of the polymer. Whether this degradation is due to chemical attack or the shearing action of the reciprocating stirrer bath used in these studies is not known at present. However, it has also been found that the GPC elution curves of fresh polymer solutions do not differ significantly from those obtained after shaking the solutions for six weeks in the stirrer bath, indicating minimal degradation over this time interval. Future studies will be conducted within a six-week period in order to minimize the effects of polymer degradation.

#### Characterization of Porosity of Porous Implant Materials Subtask 10 of Task 12135

R. E. Dehl

Porous synthetic biomaterials are currently being used as implants, where they become stabilized by the ingrowth of hard or soft natural tissues. Both the rate and the type of tissue ingrowth are affected by the porosity of the materials, and it is important to be able to characterize the porosity by reliable and reproducible methods. During the first phase of this work, which is being carried out in cooperation with the Bureau of Medical Devices, Food and Drug Administration, we have surveyed the published literature pertaining to porous polymeric implant materials and initiated studies of pore size and pore volume using mercury intrusion porosimetry. The materials currently being investigated are porous polyethylene (PPE) and a porous composite of polytetrafluoroethylene and pyrolytic carbon.

Our initial studies indicated qualitatively that, contrary to some expressed fears, mercury intrusion experiments apparently can be performed on the relatively soft composite material without distorting the pore structure by mechanical compression. During the past year we have quantified these observations by performing compressive stress-strain measurements on both materials. The composite has highly anisotropic mechanical



properties due to its laminated construction, the compression modulus being about five times greater in the direction parallel to the laminations, as compared with perpendicular compression.

The pore volume in these materials has been measured by three different methods and the pore "size" by two methods, namely mercury intrusion porosimetry and an indirect method based upon the specific surface area and specific pore volume. The surface areas have been measured both by the Brunauer, Emmet, Teller (BET) inert gas adsorption method and by the mercury porosimetry method in which the surface area is proportional to the integrated area of a pressure-volume mercury intrusion curve. Both methods agree that the PPE has a smaller surface area than the composite, but the BET method indicates a much greater difference, for reasons which are currently under investigation.

The accuracy of the mercury intrusion method for measuring pore size has been tested by performing an estimated random error analysis of the experiment and plotting volume-weighted pore size distribution curves based upon these error limits. The resulting curves show that the experimental precision is not sufficient to produce well resolved distribution curves, over much of the pressure range pertinent to these materials, but that the precision increases rapidly with increasing pressure, corresponding to smaller pores.

Quantitative studies of porosity are also being initiated, using the methods of quantitative stereology. The accomplishment of this project's objectives will be of significance to the medical device industry and medical implant standards development, as well as to the users of porous implant materials.

#### Surgical Bone Cement Modification Subtask 11 of Task 12135

J. A. Tesk, G. M. Brauer, W. Wu, and J. E. McKinney

While surgical bone cement is a major asset in orthopaedic practice, it has deficiencies that are of much concern, particularly in total joint replacement. Failure at the cement/bone or cement/implant interface is considered to be an important step in reducing the life time of such total joint replacements as those used to reconstruct knee and hip joints.

With the view that completely new bone cements are not likely to be forthcoming, we have directed our efforts to improving the presently available materials and techniques. A first effort has been to examine the potential of some less toxic new amines, proven in our lab to be more reactive with the dental resin, BIS-GMA, than amines currently employed. We have found that dialkylaminophenethanol used with benzoyl peroxide as initiator will give faster curing of bone cement. This cure time is reduced even more by addition of equimolar concentrations of benzoic acid. We have initiated efforts to reduce the heat liberated on polymerization by bone cement by investigating the substitution of the reactive but higher molecular weight dicyclopentyloxyethyl methacrylate for presently used methyl methacrylate.

Based on the results of the amine studies additional tests will be chosen from among those considered in the original protocol. One such avenue of investigation involves determining if performance may be expected to be improved by precoating of a prosthetic stem with highly cured polymer. The properties of the polymer are expected to be improved relative to properties at the interface of a stem and self-curing acrylic; the stem will be a heat sink and the lower interface temperature should inhibit obtaining an optimum cure. A precoated stem, however, will be insulated from the self-curing acrylic, the polymer itself should be solvated somewhat by the self curing monomer, and interface properties improved by the post curing of the precoat.

At present, 10 cobalt-chromium rods 3/8" diameter have been cast (courtesy, Howmedica, Inc.) and prepared for testing with polymer. Initial tests are in progress regarding comparative pushout force-displacement evaluation of coated and uncoated rods.

Dental and Medical Materials Standards  
Subtask 12 of Task 12135

J. M. Cassel, J. A. Tesk, G. M. Brauer, and N. W. Rupp<sup>1</sup>

<sup>1</sup>Research Associate, American Dental Association

Dental and medical implant standards development is strongly supported by persons in positions of Committee, Subcommittee, and Task Force Chair roles in ANSI MD 156, Dental Materials, Instruments, and Equipment, and in ASTM F-4, Medical and Surgical Materials and Devices. Additional leadership roles are fulfilled through the Chairpersons role in USA TAG ISO/TC 150, Implants for Surgery, and USA TAG ISO/TC106, Dental Materials, Instruments, and Equipment, and through participation in the Executive Committee of the ANSI Medical Device, Standards Management Board.

Considerable effort has gone into drafting four new or revised ANSI/ADA dental specifications and comparable ISO standards. These cover alloys, mercury and devices used in the preparation of amalgams.

An active role was taken in the planning for and organization of U. S. participation in the Fifth Meeting of ISO/TC 150, Implants for Surgery, held in Washington, DC.

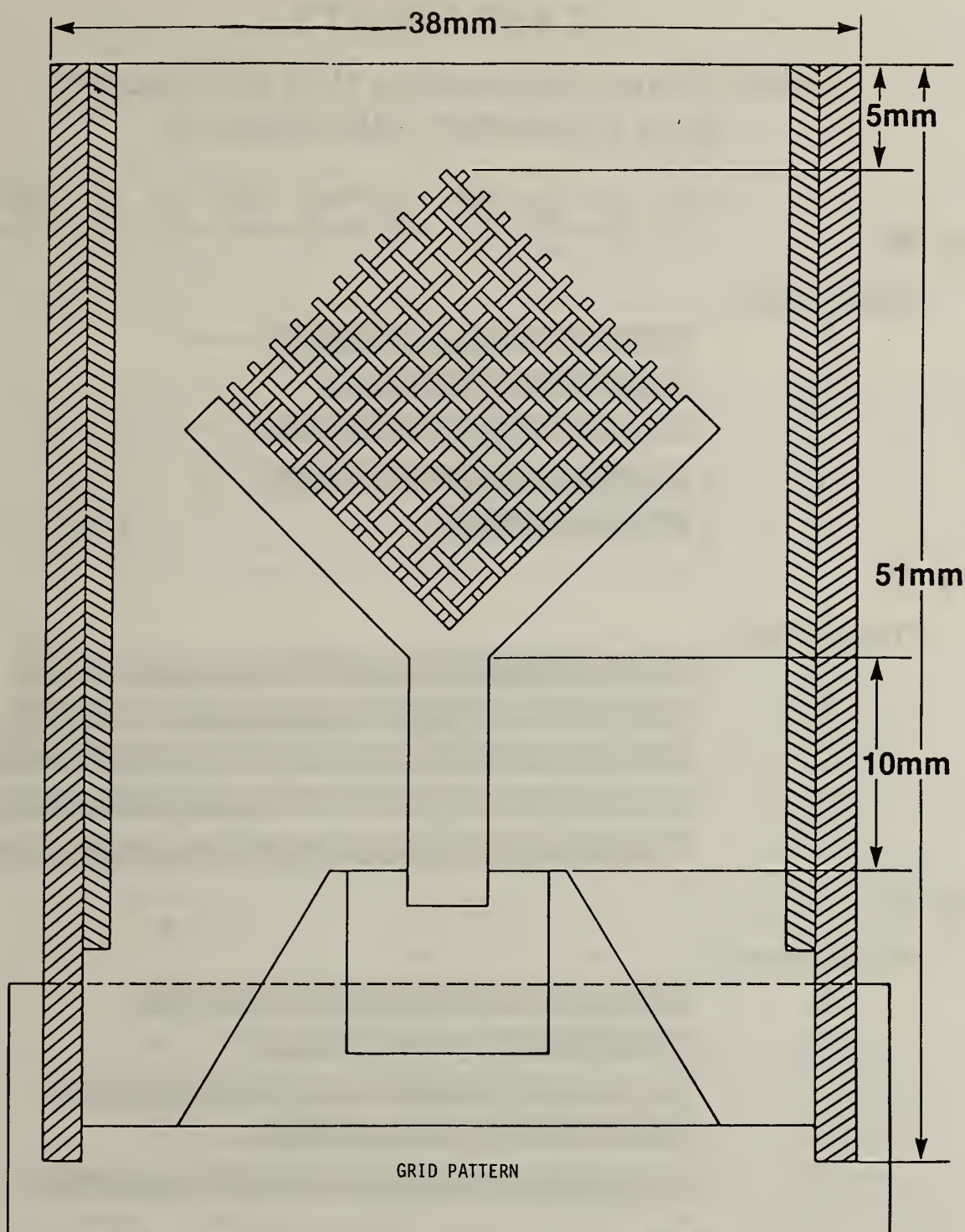


Figure 1 Grid pattern.



# CASTABILITY

USING STANDARD EVALUATION PROCEDURE  
WITH DIFFERENT INVESTMENTS

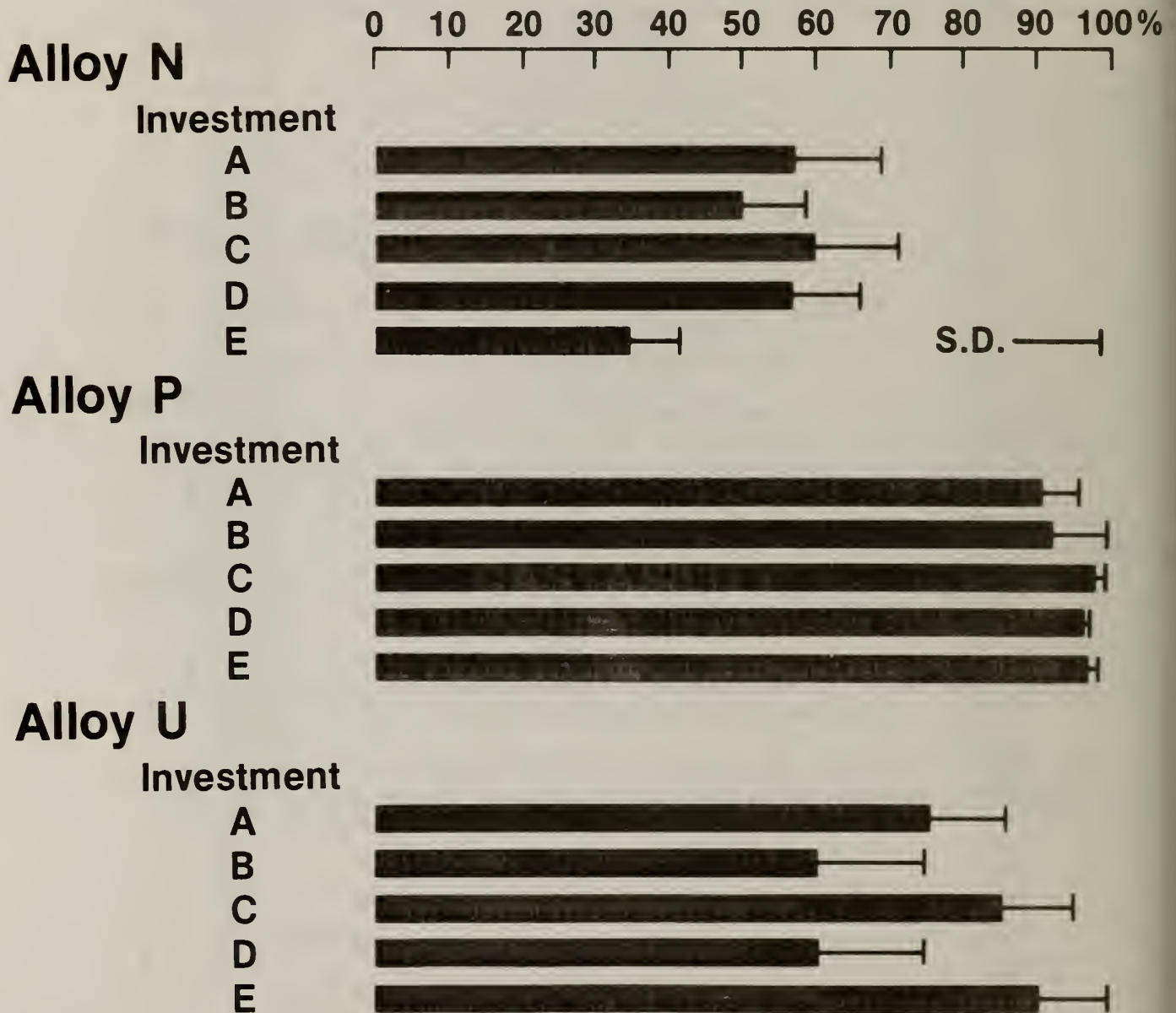


Figure 2

## MECHANICAL DURABILITY OF POLYMERS

### Task 12136

The growth in the use of polymeric materials derives from substitution for other materials as well as new applications due to the unique properties of these materials. In many applications long-term mechanical durability is critically important. The realization of increased utilization is often limited by the lack of data and models upon which to design for long-term use. Thus, the lack of adequate test methods and data for evaluation of long-term mechanical performance not only restricts applications, but also leads to over design which results in more expensive items and limits weight savings. Evaluation and control of material parameters that affect long-term performance should lead to more durable materials and, hence, reliable performance for the intended service life.

The objective of this task is to provide data, test methods, and standards for evaluation of long-term mechanical durability of polymeric materials. The approach is to identify and analyze principal failure mechanisms of commercially important thermoplastics under mechanical stress in the use environment, to determine the effects of chemical structure and fine structure morphology on mechanical properties and failure processes, and to develop constitutive relationships and models for mechanical properties to serve as the basis for accelerated test methodology and lifetime prediction.

The approach to development and verification of predictive models of mechanical performance are: (1) establish dependence of the principal failure modes of inhomogeneous deformation and crack initiation and growth on static and dynamic mechanical stress; (2) identify the principal molecular processes associated with deformation and failure and relate failure to molecular structure and fine texture; (3) evaluate the kinetic theory of bond rupture as a model for degradation of mechanical properties and for extrapolation of short-time measurements to predict long-time performance; (4) on the basis of (1), model failure by neck formation and propagation using time-dependent constitutive relations that predict the onset of inhomogeneous deformation from baseline mechanical properties characterization; and (5) expand fracture mechanics approach to viscoelastic materials to model craze and crack growth phenomena.

The National Bureau of Standards has established joint programs on mechanical durability with other Federal agencies which are fostering the application of polymeric materials in areas of national concern. For example, joint program with the Defense Advanced Research Projects Agency is concerned with development of molecular characterization techniques for mechanical degradation as the basis for nondestructive evaluation methods. Joint projects are also executed with industries. An example is the joint project with Firestone Tire and Rubber Company on the effects of processing on PET structure and properties.

Molecular Processes Associated with Mechanical Deformation and Failure  
Subtask 1 of Task 12136

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The elucidation of molecular processes and structure changes accompanying mechanical deformation and failure not only provides the basis for development of test methods for long-term performance and quality control, but also provides insight into the selection and design of materials with improved mechanical performance and durability. The semicrystalline structures found in some commonly used polymeric materials present significant challenges to characterization of molecular structure. Newly developed spectroscopic techniques involving <sup>13</sup>C nuclear magnetic resonance (NMR) and FTIR spectroscopies are used to elucidate molecular conformations in disordered material. Reorganization of polymer molecules during deformation affects mechanical performance. Identification of the molecular processes involved and the physical structures which result are the aim of the studies.

FTIR is used to determine relationships between the number of chain scissions produced by mechanical stress, the useful service life, and molecular weight and its distribution.

Chain Scission and Mechanical Durability of Polymers

Chain scission is an underlying molecular process associated with mechanical deformation and degradation. Previous work has established that infrared spectroscopy can be used to determine the number of carbon-carbon bonds that are ruptured under mechanical stress to form new chemical end groups.

We had applied this method to determine the number of chain scissions at fracture per measured free radical, the precursor to new end group formation. Our measurements, utilizing the improved signal-to-noise capability of Fourier transform infrared spectroscopy, established that the number of chain scissions per free radical was 1 to 2 orders of magnitude lower than previous estimates.

Spectral studies of chain scission have now been extended to ultra high molecular weight polyethylene damaged under fatigue loading, and to polystyrene damaged by fracturing at cryogenic temperatures. The latter study was carried out as a function of molecular weight and correlations with the electron spin resonance determinations of secondary free radical concentrations have been made.

Specimens of ultra high molecular weight polyethylene (UHMWPE) were fatigued under uniaxial deformation at various frequencies and peak stresses. The applied load varied sinusoidally in time. The fatigued specimens were examined using FTIR after failure occurred. In table 1 is shown the concentrations of carbonyl end groups found in specimens of UHMWPE fatigued at 0.002 Hz and in which the peak stress varied from 30 to



Table 1

Peak Stress (MPa)	Concentration of C=O (number per gram)
30	$1.95 \times 10^{18}$
35	$1.82 \times 10^{18}$
40	$2.03 \times 10^{18}$
45	$1.97 \times 10^{18}$

45 MPa. The carbonyl and methyl groups were the only ones that showed an increased concentration as a result of mechanical damage. The vinyl bonds did not show any measurable change, even though the initial concentrations of these groups were extremely low which would facilitate the observation of small changes in concentration. This finding substantiates our earlier conclusions that the previously reported changes in vinyl group concentrations resulted from poor sampling procedures and the initially high concentrations of vinyl groups. We also observed increases in methyl group concentrations but do not report these because of the large uncertainties that result from the strong IR absorption due to methylene wagging modes in the same frequency range.

The significant result from table 1 is that the concentration of new end groups at failure is independent of the number of cycles, peak stress level, or time-to-failure. By varying peak stress the time-to-failure and number of cycles to failure varied by two orders of magnitude. Our findings suggest that failure is associated with a critical concentration of bond ruptures and that IR measurements may serve as the basis for nondestructive test methods. Current work is aimed at substantiating the findings for different test frequencies and molecular weights.

Chain scission in a glassy polymer was examined using polystyrenes in the molecular weight range of 200,000 to 800,000 g/mol. Specimens were fractured by grinding at cryogenic temperatures and secondary free radical concentrations measured by electron spin resonance prior to warming the specimens to room temperature. The samples for infrared investigations were prepared by melt or solvent casting films of the fractured and reference material. Spectra were compared to those of the reference polymer and the increased absorption due to new end groups was converted to concentrations using literature values of the extinction coefficient. The viscosity-averaged molecular weight was also determined, and from assumptions of random chain scission the molecular weight changes were converted to number of chain scissions. In table 2 we compare the number of free radicals, the number of chain scissions by viscosity measurements, and the IR-determined number of bond scissions. For this glassy polymer the change in molecular weight and the IR measurements yield similar values of the number of chain scissions. The electron spin resonance (ESR) values are lower by a factor of 2 to 3 indicating that a secondary free radical may produce more than one chain scission. The insensitivity of the number of chain scissions to molecular weight can be related to grinding at low temperature where large scale molecular motion is prohibited.

Table 2

MW $\times 10^3$	Viscometry Ruptures number per $\text{cm}^3 \times 10^{-16}$	ESR $R'/\text{cm}^3$ $\times 10^{-16}$	IR Chain Scissions number/ $\text{cm}^3 \times 10^{-16}$
220	$17.0 \pm 3$	$4.5 \pm 2$	$17 \pm 3$
637	$11.0 \pm 3$	$6.3 \pm 2$	$22 \pm 4$
916	$15.0 \pm 4$	$5.0 \pm 2$	$24 \pm 4$

#### Examination of Drawn PET Fibers by Solid State NMR

This work is a continuation of work begun in FY81 and is a joint effort with the Firestone Tire and Rubber Company. The interest is to learn how to control shrinkage of PET fibers in tires during rubber curing while maintaining mechanical strength.

In previous  $^{13}\text{C}$  NMR studies on these materials, it became clear that a better understanding of the relationship between morphology and orientation in drawn PET fibers would be very helpful. Using the  $^{13}\text{C}$  NMR method, one could get a reasonable description of overall fiber orientation. However, temperature-dependent studies showed significant heterogeneity of molecular mobility among the oriented aromatic groups in a drawn sample. This underscored the importance of understanding the nature of the distinction between crystalline and noncrystalline phases in these materials. Several NMR techniques were applied to this question making use of magic angle sample spinning spectra, relaxation time measurements, orientational measurements, and spin diffusion measurements. Although x-ray techniques indicate rather small crystallite sizes, particularly along the C-axis (3.5 to 6 nm), calculations of crystallinity from the x-ray data contain a great deal of uncertainty.

In FY82 a different NMR approach to the question of crystallinity was undertaken. This approach was based on the phenomenon of spin diffusion (really diffusion of spin polarization). If a well-defined spin polarization gradient can be produced in a 2-phase system such as PET, and if the system can be observed for a sufficiently long time thereafter (but a time short compared to the longitudinal relaxation time,  $T_1$ ), the rate at which spin polarization equilibrium is attained will indicate the size of the domain(s) since the spin diffusion constant is approximately known.

Protons (and not  $^{13}\text{C}$ ) exhibit strong spin-diffusion characteristics. Therefore, much effort was put forth finding the optimal conditions for generating magnetization gradients between the two phases of the drawn PET fibers. This problem is not easy because very few chains, below  $T_g$ , in PET undergo significant motion on the NMR timescale of  $10^{-5}$  s; therefore, it is difficult to create polarization gradients below  $T_g$ . Above,  $T_g$ , this task is easier but the sample also changes irreversibly. Although some compromises have to be made, current efforts make use of differences in rotating frame relaxation times between the two phases in order to



establish a polarization gradient. Preliminary results suggest that equilibration times between the two phases are not a very sensitive function of post-annealing history.

In a quantitative way, this suggests that there is no significant reduction in surface area between the two phases. Moreover, annealing is not significantly changing the sum of the crystalline plus noncrystalline domain size in the direction of minimum thickness. The distances for this sum deduced from the spin diffusion rates are in range of 10 to 15 nm. This is in accord with x-ray results. The picture of drawn, annealed (at constant length) fibers is that annealing increases the regular ordering in the drawn fibers but it does not result in substantial thickening of the crystalline regions. Moreover, in annealing, only those chains which were originally well-oriented in the draw direction are involved in the perfecting of order by annealing. Orientation in the noncrystalline region remains pretty much independent of annealing with a slight disordering at high annealing temperatures. This is probably the reason that modulus tends to degrade at high annealing temperatures even though crystalline orientation remains high.

It should be noted that Dr. V. Mochel from Firestone Tire and Rubber Company spent a week at NBS working on the project in FY81 and that Dr. K. W. Zilm from Utah Research Institute spent a month in FY82 working on some of the PET proton experiments.

#### Characterization of Ultrahigh Modulus Materials

This work is aimed at developing techniques to characterize structural features of ultrahigh modulus polymeric materials. This year a collaboration effort was initiated with Professor Ian M. Ward of the University of Leeds in England. Professor Ward has extensive sample preparation facilities for producing highly drawn materials. We are exploring the possibilities that NMR may be able to obtain information about tie molecules, those molecules that bridge one crystalline lamella to another, which are regarded as essential components for achieving a high modulus. Studies are underway investigating effects of molecular weight, draw ratio, and draw temperature. One of the measures which may relate to tie molecules is longitudinal growth of  $^{13}\text{C}$  magnetization in the intermediate time regime. This magnetization has the appropriate orientation to correspond to tie molecules. In preliminary investigations to date, the number of chain segments corresponding to this magnetization is roughly proportional to the noncrystalline fraction in all drawn materials. A significant observation which lends credence to this pursuit is the smaller fraction of material associated with this magnetization in an unoriented sample where we would expect fewer tie molecules traversing the noncrystalline region.

#### Investigations of Cellulosic Materials used in Paper Making

A cooperative effort with the Bureau of Engraving and Printing is aimed at identifying more durable and less expensive substitutes for currency papers which are presently made from linen and cotton cellulosic materials. Wood pulps are a much more available source of materials but the mechanical characteristics of these papers is generally inferior. A fundamental



question is how the morphology of paper affects its mechanical properties and durability. In FY81 we used magic angle spinning (MAS)  $^{13}\text{C}$  NMR to investigate any modifications to the surface area of cotton and wood pulp materials as a result of wet beating. (Wet beating is the process whereby pulps are sufficiently plasticized in order to make paper.) One of the characteristics of the  $^{13}\text{C}$  spectra is that the presence of water in various amounts produces only minor changes in the spectra. Therefore, in an effort to understand the microstructure of cellulose better, an intensive effort was put forth to obtain more information about the interaction between  $\text{H}_2\text{O}$  and cellulose. A significant objective in these studies is to answer the question of whether disorder in native celluloses is associated with only disorder on the surface of cellulose fibrils, or disorder also exists in three-dimensional noncrystalline regions. The spin diffusion studies combined with  $^{13}\text{C}$ -MAS experiments should shed significant light on this question. To date, the principal material for study has been cotton. The transfer of magnetization between water and cellulose, via spin diffusion, has been witnessed as a function of water content. It has been established by  $^{13}\text{C}$  NMR that proton magnetization gradients in the cellulose can indeed exist, thereby leaving open the possibility that three-dimensional disordered regions exist.

The Distribution of Stresses in Craze at Crack Tips  
Subtask 2 of Task 12136

E. Passaglia

When computing any of several criteria for crack-growth (such as critical crack opening displacement or work to fracture) in crazing polymers, it is necessary to know the distribution of stresses within the craze. From this distribution the craze displacement profile may be calculated, giving crack opening displacement directly, or work to fracture by the product of stress and displacement.

Many workers have used the Dugdale model for the craze which assumes a constant stress within the craze. On the other hand, by direct determination from the electron microscopic observation of the displacement profile in either continuous crazes or crazes at crack tips, Kramer and co-workers [1,2] have shown that the stress is not constant within the craze. Most typically, it has a peak at the craze tip, and may also rise at the crack tip.

It becomes of interest, therefore to develop a means for determining the stress distribution in a craze. This may be done if the craze is modeled as a necking and drawing process. It has been shown that this leads to reasonable results [3]. In this model, in a moving crack, material at the craze tip is assumed to fibrillate, with the fibrils drawing out from the unfibrillated substrate, as the necked polymer is drawn from the unnecked in a drawing process. The rate of craze displacement thus corresponds to the rate of drawing, and the stress will be a function of this rate.

Consider now a crack with a craze zone at its tip propagating uniformly under the action of an applied stress intensity factor  $K$ . If under this condition of uniform translation the craze stress cancels the stress

singularity that would otherwise be present, the displacement may easily be calculated [4]. (It is noted that this implies a critical crack opening displacement or work to fracture criterion for crack advance.) Now denoting the displacement by  $w$ , and the crack velocity by  $v$ , from the condition of uniform translation we have

$$(\partial w / \partial t)_X = -v (\partial w / \partial X)_t \quad (1)$$

where  $X$  is a position coordinate. With an origin at the crack tip and coordinate  $\xi$ ,

$$\partial w / \partial t_X = v \partial w / \partial \xi . \quad (2)$$

From the displacement,  $\partial w / \partial \xi$  is easily evaluated. This gives

$$\partial w / \partial \xi = C_e / 2\pi \int_0^\alpha \sigma(\xi) (\xi / \zeta)^{1/2} d\zeta / \xi - \zeta , \quad (3)$$

where  $C_e$  is the plane strain compliance of the uncrazed material,  $\alpha$  is the craze length,  $\sigma(\xi)$  is the stress distribution in the craze, and  $\zeta$  is an integration variable. Now, since the stress is assumed to be a function of the rate of change of displacement at the point  $\xi$  we have using Eqs. (2) and (3) a form of integral equation for the stress distribution. A solution algorithm is the following:

- (1) Assume a relation between stress and rate of change of displacement. From the hypothesis that crazing may be modelled as necking, this relation may be obtained for curves of yield and drawing stress as functions of the rate of drawing.
- (2) Assume a stress distribution and calculate  $\partial w / \partial \xi$  from Eq. (3).
- (3) From Eq. (2), and the assumed relation between stress and rate of draw, calculate  $\sigma(\xi)$ . This should be the same as the assumed stress distribution in (2).

Several attempts have been made at such a solution with these preliminary and tentative results.

- (1) A uniform stress distribution does not work, which is not surprising.
- (2) A stress distribution, which has a peak at the craze tip, is constant over most of the craze, and drops to zero at the crack tip, gives a rough approximate solution to the problem. Work on this problem will continue.

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[3] Verheulpen-Heymans, N. *Polymer* 21: 97; 1980.

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A New Test Method for Environmental Stress-Crack Resistance  
Subtask 3 of Task 12136

J. M. Crissman and L. J. Zapas

We reported previously (Polymer Science and Standards Division 1981 Annual Report) that over the past several years there has been renewed interest in the development of a new test method for determining the environmental stress-crack resistance (ESCR) of ethylene based plastics. As part of our studies concerned with long time behavior, durability, and fracture of polyethylenes, we have examined a number of possible test methods which yield information concerning ESCR. One of these methods we propose as a viable alternative to either of the test methods currently recommended by ASTM for determining ESCR. The proposed new test method has advantages over existing methods. (1) The specimens are maintained in a fixed and constant geometry. (2) The testing time is reduced. (3) The experimental scatter in the data is reduced.

The proposed new test combined features of the two most widely accepted test methods for ESCR, ASTM D-1693 and ASTM D-2552. The specimen is bent around a metallic form having a fixed radius of curvature. At the same time it is subjected to a constant applied load at an elevated temperature. During the past two years work has proceeded to determine an optimum set of test conditions for polyethylenes having widely different molecular weights. Test variables being considered are the specimen thickness, bend radius, applied load, and temperature. Four different polyethylenes ranging in molecular weight from  $10^5$  to  $4 \times 10^6$  have been used in this work. Based upon the test results for more than 400 specimens the following set of test conditions was chosen.

Specimen Thickness	0.100 to 0.125 cm
Bend Radius	0.55 cm
Applied Stress	5 MPa
Temperature	60 to 75 °C

A description of the test method, as well as a summary of the test results, including the appropriate statistical data, was presented before Committee D-20.12.03 of ASTM at their June 1982 meeting in Toronto, Canada. Subcommittee D-20.12.03 is currently in the initial stages of forming a task group to consider carrying out a round-robin test using the proposed new test method.

Creep and Recovery of UHMWPE at Very Small Deformations: A New One-Dimensional Constitutive Equation  
Subtask 4 of Task 12136

L. J. Zapas and J. M. Crissman

Since the early work on the mechanical properties of natural polymeric materials well over one hundred years ago [1,2] it was found that reproducible data could be obtained only after the specimens had been mechanically preconditioned. Leaderman in his classical publication on the "...Properties of Filamentous Materials..."[3] reported that even for synthetic polymers the Boltzmann superposition could be obtained only



when the materials were subjected to mechanical preconditioning. The necessity of preconditioning the material raises questions as to what one measures as material properties of the virgin or unconditioned polymer. Another difficulty has been the inability of the BZK Theory [4] to describe quantitatively the two-step stress-relaxation experiments where the second step is smaller or equal to one half the value of the first step.

To better understand this behavior we have obtained data on unconditioned specimens of an ultra high molecular weight polyethylene (UHMWPE) which were subjected to a variety of different strain histories in uniaxial extension. The observed behavior led us to a one dimensional constitutive relation which describes very well all of our experimental results. In the new derivation, the assumption is that the undistorted state of the material depends upon the stress history. This means that the strain which the material itself sees is not that which the observer sees. For very small deformations, of the order of one percent and below, the constitutive relation is given by the following equation:

$$\varepsilon(t) - \phi \left( \int_{-\infty}^t g(\sigma(\xi)) d\xi \right) = J(\sigma(t), 0) + \int_{-\infty}^t J_x(\sigma(\xi), t-\xi) d\xi, \quad (1)$$

where  $\varepsilon(t)$  is the strain the observer sees,  $\sigma(t)$  is applied true stress,  $\phi(\cdot)$  is a functional, and  $J(\sigma, t)$  is a nonlinear compliance.  $J_x(\cdot, \cdot)$  denotes the partial derivative of  $J(\cdot, \cdot)$  with respect to the second argument. When  $\phi(\cdot)$  is zero and  $J(\sigma, t)$  is linear in  $\sigma$ , equation (1) reduces to the Boltzmann equation. The functionals  $\phi$  and  $J$  can be obtained from a series of creep and recovery experiments.

We have carried out such a series of experiments on the UHMWPE and it is found that the functions  $\phi$  and  $J$  can be represented rather well by the expressions

$$\phi \left( \int_0^t g(\sigma(\xi)) d\xi \right) = \left( \int_0^t g(\sigma(\xi)) d\xi \right)^{1/3}, \quad (2)$$

and

$$J(\sigma, t) = f_1(\sigma) + f_2(\sigma) t^{1/3} \quad (3)$$

Relations (2) and (3) along with equation (1) give interesting prediction that recovery data, obtained from a series of creep experiments done at constant stress but different values of the duration of the step, can be superposed onto a master curve with predetermined shift factors along both the strain and time axes. This was done and the data points on the resultant master curve formed a very narrow band of the order of 10 percent or less, which is as good as the reproducibility of the creep curves from specimen to specimen. We have also calculated the behavior for multistep creep and recovery experiments and the agreement was within 2 percent of the experimental values.

Since Eq. (1) is nonlinear, it cannot be inverted in order to determine the stress as a function of the strain history. However, the consistency of Eq. (1) can be determined from experiments where the stress is measured

as a function of the strain history, by assuming that, infinitesimally in time, the motions are obtained from constant stress experiments. This was done for single- and two-step stress-relaxation experiments and the predicted strains were within a few percent of the actual applied strains. For a two step in strain experiment, where the second step was very close to half the strain of the first step, the BZK prediction gave results for the second step which were higher by 45 percent, while the strains calculated using Eq. (1) fell within 3 percent of the experimental values. The proposed viscoelastic equation appears to have the necessary elements in order to be capable of describing quantitatively both the creep and recovery behavior of a wide range of materials.

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A Study of the Morphology and Mechanical Properties, and Their Dependence on Thermal History and Processing of Ultra High Molecular Weight Polyethylene Subtask 5 of Task 12136

J. M. Crissman and F. Khoury

Ultra high molecular weight polyethylene (UHMWPE) is used in the manufacture of a variety of orthopedic joint prostheses. One factor which limits the lifetime of a prosthesis is the durability of the UHMWPE component. The length of time between device implantation and failure depends upon time dependent processes which result from the clinical loading environment. In clinical use, failure of the polymeric component has been reported to occur as a result of creep, wear, fatigue associated with wear, and even fracture. Both the mechanical properties and durability are determined by the polymer chemistry and morphology related features. Factors such as crystallinity, orientation, spherulite size and texture, as well as molecular weight and molecular weight distribution all influence mechanical performance. Under contract with the Bureau of Medical Devices, Food and Drug Administration, we are in the third year of a study concerned with the relationship between the morphology of UHMWPE and the mechanical behavior. An important aspect of this work is the determination of the mechanical behavior variability which can be brought about by changes in processing conditions.

A summary of the earlier work done in this project is contained in the Polymer Science and Standards Division 1981 Annual Report. The initial stages of the work dealt mainly with (1) characterization of the raw polymer powder, (2) establishment of procedures for compression molding, under vacuum, sheets and cylinders of the UHMWPE, (3) characterization of



the processed polymer, and (4) initiation of preliminary experiments on the creep, stress-relaxation, and fatigue behavior of UHMWPE. We have previously reported on the morphology, density, and uniaxial stretching and recovery of compression molded sheets made from a UHMWPE polymer (UH-1) having an intrinsic viscosity of  $\sim 25$  dl/g ( $MW \sim 4 \times 10^6$ ). The sheets were molded at 200 °C and then cooled to room temperature at  $\sim 1$  °C/min. The density of these sheets was in the range 0.934 to 0.936 g/cm<sup>3</sup>, the higher density corresponding to a weight percent crystallinity,  $\chi$ , of 59.7 percent. Sheets which were quenched from the melt into cold water have a density of 0.923 g/cm<sup>3</sup> ( $\chi = 51.5$  percent). In order to determine whether appreciable higher crystallinities can be achieved with this polymer, sheets of the slowly cooled material were annealed in nitrogen at successively higher temperatures in the range 125 to 135 °C. The highest density attained was 0.942 g/cm<sup>3</sup> ( $\chi = 63.4$  percent).

Since molecular weight can also be an important factor in determining mechanical behavior, in FY82 the work was expanded to include a lower molecular weight UHMWPE (UH-2) having an intrinsic viscosity of  $\sim 18$  dl/g ( $MW \sim 2 \times 10^6$ ). Sheets of the UH-2, prepared under the same three sets of conditions described for the UH-1, had densities which ranged from 0.925 g/cm<sup>3</sup> ( $\chi = 52.2$  percent) for the quenched polymer to 0.953 ( $\chi = 70.7$  percent) for the annealed polymer. Clearly, the crystallinities of the molded sheets of the lower molecular weight polymer are not greatly different than those of the UH-1 polymer.

The densities (crystallinities) of the compression molded sheets of both polymers are comparable to those of commercial prostheses. The densities of specimens cut from various regions of five acetabular cups and five tibial plateaux were determined, and were found to fall in the range 0.923 to 0.953 g/cm<sup>3</sup>, which spans the entire range found for the compression molded UH-1 and UH-2. It should be borne in mind, however, that the prostheses were subjected to sterilization by irradiation which may have effected their densities.

In addition to measuring the density of the sheets of UH-2 molded at 200 °C and slowly cooled to room temperature, we observed the following similarities with the sheets of UH-1. First, a memory of the granular texture of the raw polymer is retained in the molded specimens. Second, specimens stretched uniaxially at 23 and 37 °C did not exhibit necking, and showed considerable recovery when released at strains below the breaking strain. For example, specimens stretched at a strain of  $\sim 0.2$ /min to strains of 2 and 3, and which were then released, had, after 24 hours storage at room temperature, residual strains of 1.09 and 1.86, respectively. Wide-angle x-ray diffraction patterns of such specimens revealed the presence of reflections associated with the monoclinic polymorphic form of polyethylene in addition to the reflections associated with the predominant orthorhombic form. The particular aspect of the deformation of sheets of UH-1 and UH-2 which is currently being investigated is the apparent preferential deformation of the specimens (during the early stages of drawing) at boundaries which delineate the "interfaces" between the "sintered grains" of raw polymer.



In the area of mechanical properties studies, work centered on the characterization of the creep and stress-relaxation behavior of both the UH-1 and UH-2 polymers as a function of thermal treatment. Particular emphasis was placed on single and multi-step creep recovery experiments at very small deformations in uniaxial extension. It was found that, even at levels of strain of 0.001 and below, the stress-strain behavior is nonlinear and the recovery behavior cannot be described by the Boltzmann Superposition Principle. To better understand the behavior of the UHMWPE a series of creep recovery experiments was done on unconditioned specimens in which either the applied stress was maintained constant and the duration of the creep step was varied, or the duration of the creep step was held constant and the applied stress was varied. The observed behavior led us to a new one dimensional constitutive relation which describes very well all our experimental results and the details of which are described elsewhere in this Annual Report.

Work was also continued to characterize the environmental stress-crack resistance of the two UHMWPE polymers. It was found that in general the slowly cooled UH-1 and UH-2 had a longer lifetime in the surface active agent than did either the quenched or annealed UH-1 and UH-2. Moreover, the ESCR of the UH-2 was better than that of the UH-1 under the same set of test conditions.

#### The Effects of Mechanical Deformation on Glassy Polymers Subtask 6 or Task 12136

G. B. McKenna and A. J. Kovacs (C.R.M.)

According to Struik [1], large deformations of aged polymer glasses can result in erasure of the prior aging. From his experimental results, Struik concluded that large stresses (or deformations) enhance the molecular mobility of the aged glass to the point that the mechanical properties are similar to those of a freshly quenched glass. He hypothesized that the deaging of a glass should be accompanied by changes in (free) volume of a magnitude appropriate to the enhanced mobility. We refer to these as structural effects, and to date there has been no experimental confirmation of them.

Deformation of compressible solids by tension and compression results in relatively large changes in volume (first order effects) [2]. On the other hand, torsional deformations are predicted from finite elasticity theories to result in much smaller volume changes (second order effects) [3]. We refer to these as mechanical effects. Because the volume changes expected in torsion are much smaller than those accompanying tension or compression, this geometry is more suitable to studying the effects of deformation on the structure of polymer glasses.

There are two major objectives for this project: the measurement of the effect of torsion on (a) the volume of a glassy sample and (b) on its molecular mobility. As for the second theme, it is of particular importance to determine if any variation of the molecular mobility is accompanied by a dilation when deaging (destabilization) is provoked by a deformation greater than a critical value. In the case of a positive response to this question, one must then determine the magnitude of the dilation in subtracting out any mechanically induced volume changes due

to the torsion. If the response is negative, we will attempt to determine the possible origin of the destabilization and the parameters which control it.

In order to accomplish the objectives, we have spent the past year in building and perfecting a torsional dilatometer (TD). With the help of this instrument we will be able to determine the effects of torsion on the volume of polymer glasses (a) in the absence of any destabilization (mechanical effect) and (b) when the deformation is accompanied by a simultaneous increase in molecular mobility (structural effect).

The apparatus has been conceived to be able to measure simultaneously, the torque, the normal force and the variation of the volume of a sample subjected to torsional deformations controlled with precision, while the length of the sample is held constant. The dilatometer is filled under vacuum with mercury through a capillary having a calibrated cross section. This is illustrated schematically in figure 1.

An electric servo-motor is used to turn the sample (fig. 2). The motor is commanded by a digital servo-system represented schematically in figure 3. The system permits the performance of single- and multiple-step stress relaxation experiments at strains varying from  $\gamma = 0.001$  to  $0.25 \pm 8 \times 10^{-5}$ . The maximum time required to introduce the step is less than 1 second. Constant rate of deformation experiments can also be carried out.

The temperature of the dilatometer is maintained constant by circulation from a water bath maintained to  $\pm 1/500$  °C. This precision is necessary to give a sensitivity of the dilatometer to relative volume changes of the order of  $\pm 10^{-6}$ . The accuracy on the torque is  $\sim \pm 3.5$  percent.

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#### Mechanical Relaxation of Liner Materials in Acetic Acid Subtask 7 of Task 12136

J. C. Phillips

Polymers of varied chemical constitution and design are increasingly used as barrier materials in hazardous materials storage ponds and landfills. The essential purpose of these materials is to prevent or impede the leakage of liquid waste products into the underlying soil and ultimately polluting the groundwater. In order to evaluate the efficacy of liner materials one has to better characterize the transport and mechanical properties behavior of these polymeric materials. The initial investigation addressed the former problem using low and high density polyethylene and the latter problem has been studied using stress relaxation measurements to test the strain performance of three



liner materials (high density polyethylene, HDPE; chlorinated polyethylene, CPE; polyvinyl chloride, PVC) both in air and acetic acid.

The experimental data for stress relaxation were obtained at temperatures of 30, 50, and 72 °C. At the latter temperature (72 °C) stress relaxation experiments were performed on HDPE as a function of elongation and concentration of acetic acid/H<sub>2</sub>O mixtures. Environmental stress cracking (ESC) experiments at 60 and 90 °C were done for HDPE using acetic acid and Igelpal as ESC agents. Additional experiments of recovery were also performed for the three linear materials. In air at 30, 50, and 72 °C, HDPE, PVC, and CPE exhibited a normal relaxation behavior over the experimental time and strain range, i.e.,

$$\log E(t) = \log K + \alpha \log t$$

where K is a function of strain  $\epsilon$  and  $\alpha$  is the slope of the log-log plot. For HDPE the slope shows little if any variation with temperature while the slope for PVC is slightly more negative and CPE has an even greater negative slope. In acetic acid the modulus was represented as a function of the characteristic time,  $t-t_0$ , of the sorption process ( $t_0$  = the time for initially bringing the liquid in contact with the sample), i.e.,

$$\log E(t) = \log K' + \beta \log (t-t_0)$$

At 30, 50, and 72 °C,  $\beta$  approximately equals  $\alpha$  for HDPE. At 72 °C, the modulus for CPE was not measurable due to an extremely rapid drop in modulus to zero immediately after stretching the sample. The only significant changes of modulus in acetic acid for PVC versus that in air also occurred at 72 °C for a strain of  $\epsilon = 0.89$ .

This investigation attempted to show how the relaxation modulus may be used as a distinguishing parameter for different liner materials under the influence of a given stress relaxation modulus, i.e., the ratio of the modulus in liquid to that in air versus time. Further refined studies may show this parameter to be quite useful in characterizing the mechanical relaxation of potential liner materials.

#### Crystal Growth Kinetics and the Lateral Growth Habits of Polyethylene Crystals

Subtask 8 of Task 12136

E. Passaglia and F. Khoury

It is well known that when polyethylene crystals are grown from solution they become more elongated in the direction of the *b* crystallographic axis the higher the temperature of growth. At high temperatures the crystals are bounded laterally by (110) and (200) crystallographic faces. The latter faces become longer relative to the (110) faces the higher the crystallization temperature. At low temperatures and in some solvents, notably xylene, the (200) faces are not present. The crystals are bounded only by (110) faces, and they exhibit the familiar lozenge habit. The ratio of the length of the crystal in the *b* crystallographic direction to its length in the *a* crystallographic direction, which we



denote by  $\bar{r}$ , the aspect ratio, is thus a measure of the habit of the crystal. The value of  $\bar{r}$  ranges from about 0.66 for the lozenge habit to five or higher at high temperatures in poor solvents.

At steady state growth,  $\bar{r}$  is related to the rates of growth normal to the (110) and (200) faces of the crystal by the simple equation

$$\bar{r} = G^{110}/(\cos\theta G^{200}), \quad (1)$$

where  $G^{110}$  and  $G^{200}$  are the rates of growth normal to the two faces, and  $\theta$  is the angle between the  $\underline{b}$  direction of the crystal and the normal to the (110) face. Since  $\bar{r}$  varies with temperature,  $G^{110}$  and  $G^{200}$  must have different temperature dependencies. The growth rate  $G$  depends upon several material parameters, the most important of which are the surface energies, and several theoretical parameters, most important among which are the length of the substrate for nucleation,  $L$ , in regime I crystallization and  $\phi$ , the fractional assignment of the free energy of crystallization to forward and backward reactions in the stem deposition process in both regimes I and II.

An analysis of the temperature dependence of crystal habits on the basis of Eq. (1) allows the possibility of investigating the values of the various parameters--particularly the determination of the relative values of surface energies associated with stem deposition and folding for the two crystal surfaces, and the effect of  $\phi$  upon the analysis.

Writing Eq. (1) explicitly we obtain for regime I crystallization ( $r_I$ ) and regime II crystallization ( $r_{II}$ ):

$$\ln r_I = \ln C_I + \ln \frac{L_{110}}{L_{200}} + \frac{2(a/2)b\phi\sigma_e^{110}}{kT} (1-\rho) \quad (2a)$$

$$+ \frac{4d_{110}\sigma_e^{110}\sigma^{110}}{\Delta h\Delta T \quad kT/T_d^0} \frac{a/2}{d_{110}} \gamma \rho^{-1}$$

$$\ln r_{II} = \ln C_{II} + \frac{(2\phi-1)(a/2)b\sigma_e^{110}}{kT} + \frac{2d_{100}\sigma_e^{110}\sigma^{110}}{\Delta h\Delta T k \quad T/T_d^0} \frac{a/2}{d_{110}} \gamma \rho^{-1}, \quad (2b)$$

where the symbols have the following meaning:

$C_I, C_{II}$ : ratios of lattice parameters (slightly temperature dependent).

$L_{100}, L_{200}$ : The length in which one nucleation event occurs for the (110) and (200) faces in regime I crystallization.

$a, b, d_{110}$ : The lengths of the  $a$  and  $b$  axes, and the (110) interplanar spacing in the crystal.

$\sigma^{110}, \sigma_e^{100}$ : The lateral and end surface free energies associated with the deposition of a stem and folding of the chain on the (110) surface of the crystal.

$\rho$ :  $\sigma_e^{200}/\sigma_e^{110}$

$\gamma$ :  $\sigma^{200}/\sigma^{100}$

$\Delta h$ : Heat of fusion of extended chain crystal, per unit volume.

$T_d^0$ : The dissolution temperature of the extended chain crystals for the given molecular weight and solvent system.

$\phi$ : Parameter that assigns a fraction of the free energy of crystallization to the forward reaction and the remainder  $(1 - \phi)$  to the backward reaction in each deposition step.

Before analyzing experimental data according to Eqs. (2a) and (2b) some decision must be made about  $L_{110}$  and  $L_{200}$ . First, if these correspond to the lengths of the respective crystal edge, then it is easy to show that growth rates are exponential, and not linear as observed experimentally. In order to obtain linear growth,  $L$  has to be a constant. Second, whatever the physical significance of  $L$ , we have no basis for assigning a different value to  $L_{110}$  and  $L_{200}$ . Hence we take them to be equal.

The analysis was carried out on data by Blundell and Keller [1] and Valenti and Pedemonte [2] for the crystallization of Marlex 6009 in xylene at various temperatures and in 0.01 percent and 0.1 percent solutions. This is the most extensive data set available for which  $T_d^0$  is known as a function of concentration and molecular weight.

The results are as follows:

(1) If  $\gamma = 1$ , i.e., if the lateral surface energy for deposition on (200) is the same as that for deposition on (110), and if  $\rho$  is not temperature dependent, no fit can be obtained for any values of  $\rho$ . This holds for both regimes and for all values of  $\phi$ . This means that at least two parameters for any given  $\phi$  are necessary to fit the data. Two parameters can be obtained in the following two ways: (a)  $\gamma = 1$ ,  $\rho$  is temperature dependent,  $\rho = \rho_0 (1 + CT)$ ; (b)  $\gamma \neq 1$ ;  $\rho \neq 1$ ; but both are temperature independent.

(2) Data analysis for case (a).

Analysis of the data in this case gives the following results:

(a) The value of  $\rho_0$  depends upon the value of  $\phi$  chosen for the analysis, and the crystallization regime assumed to control growth. However, in all cases, at a reference temperature of 338 K,  $\rho_0 > 1$  its value ranging from 1.01 to 1.1 depending on  $\phi$  and the solution concentration of the data set. The temperature coefficient is positive in all cases except  $\phi = 1$ , where it is small and negative.

It is argued that the temperature coefficient should be negative, since as temperature increases, the polyethylene lattice tends toward the hexagonal where the distinction between (110) and (200) planes disappears.

(3) . Analysis in case (b).

In this case,  $\phi$  has striking effects. For regime II analysis, at  $\phi = 1/2$ ,  $\rho$  and  $\gamma$  show discontinuities. For the regime I analysis, at  $\phi = 0$ ,  $\rho$  becomes infinite and  $\gamma$  becomes zero. The only consistent data set are obtained at  $\rho = 1$ . Here  $\rho$  has values that range from 1.1 to 1.2. However,  $\gamma$  has values slightly greater than unity for regime I analysis and slightly less than unity for regime II analysis.

(4) The effect of solution concentration.

The data chosen for analysis were obtained at concentrations of 0.01 percent and 0.1 percent. This change in concentration changes  $T_d^0$  from 377.9 K to 378.5 K for the 0.01 percent and the 0.1 percent concentrations, respectively. The change in  $r$  with concentration predicted by kinetic theory is exactly the opposite of that observed. At a constant temperature,  $r$  is predicted to decrease with increase of concentration; the data of Blundell and Keller and Valenti and Pedemonte show it to increase. If these data are accepted as correct, the results would indicate changes in  $\gamma$  and/or  $\phi$  with concentration.

(5) Conclusions:

The following tentative conclusions may be drawn from the analysis

- (a)  $\sigma_e^{200} > \sigma_e^{110}$ --The fold energy for deposition of stems on the (200) face is of the order of 10 percent greater than that for deposition on (110).
- (b)  $\sigma^{200} \approx \sigma^{110}$ --The lateral surface free energies are approximately equal. The actual relative values cannot be established until the crystallization regime question for these crystals is settled, and the theoretical question of the value of  $\phi$  is answered.
- (c) It is very probable that  $\sigma_e^{200}$  has a slightly different temperature dependence than  $\sigma_e^{110}$ .
- (d) The values of  $\phi$  and  $L$  are outstanding problems in the kinetic theory of polymer crystallization.
- (e) The kinetic theory predicts a different concentration dependence of  $r$  than that observed by Blundell and Keller and Valente and Pedemonte unless the surface energies change with concentration and the change is different for different crystal faces.



(f) While no specific analysis was carried out on the effects of molecular weight, some remarks on its effect may be made. For a given solvent and concentration, theory predicts an increase of  $T_d^0$  with molecular weight. Hence, at constant temperature at a given concentration,  $r$  should decrease with increase of molecular weight, absent any change of  $\rho$  or  $\gamma$  with molecular weight. The data in references [1] and [2] show an increase of  $r$  with molecular weight. The opposite effect is found by Takamizawa et al. [3] in xylene, and by Khoury [4] in other solvents.

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[2] Valenti, B.; Pedemonte, E. *La Chimica e Industria* 54: 112; 1972.

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The Morphology of Polyethylene Crystals Grown From Solution  
Subtask 9 of Task 12136

F. A. Khoury and L. H. Bolz

The lateral growth habits and nonplanar conformations of polyethylene crystals grown from dilute solutions are known to vary depending on the crystallization temperature, other factors remaining equal (solvent, mol. wt., polymer concentration).

We have previously reported that crystals exhibiting "truncated" lateral habits and having aspect ratio  $r^*$  in the range 1.6 to 6 were grown from heptyl acetate and dodecanol. The following effects of temperature, molecular weight, and solvent on the aspect ratio of crystals were observed. (1) As expected, for a given molecular weight, concentration, and solvent, the higher the crystallization temperature the higher  $r$ . In addition, whereas the crystals with low  $r$  exhibited well defined (110) and (200) faces, the (200) "edges" of the lamellae tended to become curved, and all the more pronouncedly so, the larger  $r$ . (2) For a given crystallization temperature, concentration, and solvent, the higher the molecular weight, the smaller  $r$ . (3) For a given crystallization temperature, concentration, and molecular weight,  $r$  was larger for crystals grown from heptyl acetate than dodecanol, which is a poorer solvent. These results clearly illustrate the strong dependence of  $r$  on the undercooling  $\Delta T$ .

Our current investigations are aimed primarily at determining the nature of the conformations of crystals of various fractions using scanning transmission electron microscopy and selected area electron diffraction. Our earlier studies had been limited to an examination of crystals of Fraction I (Mol. wt. 11,400) grown from dodecanol at 115 °C.

$r^*$  = ratio of the dimensions of the lamellae parallel to the [010] and [100] directions.

These crystals had an aspect ratio  $r \sim 6$ . The main feature of interest was that the majority of the crystals had asymmetric conformations, i.e., the two halves of the lamellae situated on opposite sides of the long axis were not mirror images of one another. More recently, we have found this to be the case for three other species of crystals with smaller aspect ratios. These were: (1) Crystals of Fraction I,  $r = 3.5$  (grown from heptyl acetate at 105 °C); (2) Crystals of Fraction I,  $r = 3.2$  (grown from dodecanol at 112 °C); and (3) Crystals of Fraction III, Mol. wt. = 100,500,  $r = 2.5$  (grown from heptyl acetate at 112 °C). It remains to be determined how widespread is the manifestation of this phenomenon among the crystals (of the various fractions) whose aspect ratio is in the range  $r = 1.6$  to 6.

Interest in asymmetric crystals such as the ones we have observed so far, stems from the not unreasonable speculation that they have features in common with, and hence will shed some light on, the nature of the experimentally less accessible constituent lamellae in axialitic and spherulitic structures formed in bulk polymer.

#### The Energies of (110) and (200) Folds in Polyethylene Crystals Subtask 10 or Task 12136

F. A. Khoury, J. Mazur, and B. M. Fanconi

The energies of (100) and (200) folds in polyethylene crystals are of interest in connection with the elucidation of the origins of two features of the morphology of solution-grown as well as melt-grown crystals. These two features are: (1) The occurrence of fold staggering resulting in the formation of hollow pyramidal, tent-like, or otherwise nonplanar lamellar crystals; and (2) the dependence of the lateral growth habits of the crystals on the crystallization conditions. The particular feature of interest in the latter context is the dependence of the aspect ratio  $r$  of the lamellae on the crystallization temperature (see previous Subtask, "The Morphology of Polyethylene Crystals", F. A. Khoury and L. H. Bolz).

As an initial step in examining the possible relationships between the above mentioned morphological features and the (110) and (200) fold energies, minimum energy conformation for models of such folds were computed. Adjacent reentry was assumed for the following three cases: (1) Isolated (110) and (200) folds at the surface of a lamella; (2) (110) and (200) folds surrounded by and interacting with kindred folds situated in the same and adjoining (110) and (200) planes, respectively. In (1) and (2), the stems bridged by the folds were assumed to be at right angles to the crystal surface; and (3) (200) folds surrounded by neighboring (200) folds packed in a staggered manner, i.e., the crystal surface was assumed to be (201).

The computations of fold energies involved the summation of pair-wise interactions calculated as a function of interatomic separations  $r$  for both inter and intra molecular interactions. The nonbonded carbon-carbon, carbon-hydrogen, and hydrogen-hydrogen interactions were assumed to be represented by Buckingham type potential functions ( $E = Ae^{-Br} - C/r^6$ ).



Interactions for  $r > 0.6$  nm were neglected. The empirical parameters (A, B, and C) of the Williams IV set were used. Additional energy contributions due to bond angle and bond stretching deformations, as well as due to rotations around backbone bonds were also computed. A generalized Urey-Bradley force field was assumed for these intramolecular interactions. The minimum energy fold conformation was determined in each case using the Newton-Raphson iterative procedure. Only the atoms in the folds were allowed to change in the energy minimization process, the coordinates of the carbon atoms in the stems underlying the folds were held fixed. The polyethylene unit cell parameters used were  $a = 7.4\text{\AA}$ ,  $b = 4.95\text{\AA}$ ,  $c = 2.536\text{\AA}$ ,  $\alpha = \beta = \gamma = 90$  deg, setting angle  $\theta = 48$  with respect to the b-axis.

In the case of isolated folds (Case I above) the (200) fold energy was lower than that of the most favorable (110) folds by  $\sim 1$  kcal/mole (in close agreement with [1]). In contrast, when interfold interactions were taken into account (Case II) the (110) fold energy was  $\sim 3$  kcal/mole lower than the (200) fold energy. This difference was determined from a comparison of the most favorable lateral packing arrangement of (110) folds with that of (200) folds. Staggering of (200) folds (case III, lamellar surface (201)) results in a lowering of the fold energy. The energy corresponding to the most favorable lateral packing of staggered (200) folds was  $\sim 0.9$  kcal/mol lower than that for unstaggered (200) folds.

It is interesting that the computations of fold energies summarized above, in which the interactions between neighboring folds are taken into account (Cases II, III), indicate that the energy of (200) folds is higher than that of (110) folds. This result of the comparison of the most energetically favorable models for each type of fold, and the results of the analysis (based on the kinetic theory of polymer crystal growth) of the changes in the lateral growth habits of polyethylene crystals grown from xylene solutions as a function of undercooling, are in qualitative agreement (see Crystal Growth Kinetics and the Lateral Growth Habits of Polyethylene Crystals, E. Passaglia and F. A. Khoury).

Calculations are at present being carried out to determine the effect of staggering on the energy of (110) folds.

[1] Corradini, P. et al. *Macromolecules* 4: 770; 1971.

#### Durability of Elastomers Used in Geothermal Energy Production Subtask 11 of Task 12136

R. W. Penn

The objective of this project was to develop a rational technique for measuring the rates of breaking and formation of chemical bonds affecting the mechanical properties of elastomeric sealant materials aging under geothermal down-well conditions. The project was to include a theoretical and experimental approach following the treatment developed by Tobolsky, et al. as modified by Kearsley and reported in detail previously. This



treatment relies upon a simple modification of the kinetic theory of rubber elasticity

$$\lambda f_{\lambda} - \mu f_{\mu} = NkT[g(\lambda) - g(\mu)] \quad (1)$$

where  $\lambda$ ,  $\mu$  are stretches,  $f_{\lambda}$  and  $f_{\mu}$  are the forces acting on the faces of the prism perpendicular to stretch  $\lambda$  and  $\mu$  respectively,  $k$  is Boltzmann's constant,  $T$  is absolute temperature.  $g(\lambda)$  is an arbitrary function which is to be measured by experiment. This equation is consistent with a recent phenomenological theory of Valanis and Landel if we equate their  $\lambda w'(\lambda)$  with our  $NkTg(\lambda)$ . In the case of simple extension,  $f_{\mu}$  and  $f_{\nu}$  acting on the force free sides of the sample are zero,  $\mu$  and  $\nu$  are equal to  $\lambda^{-1/2}$  (because of the assumed constant volume) and Eq. (1) becomes

$$\lambda f = NkT h(\lambda) \quad (2)$$

where  $f$  is the tensile force producing the stretch  $\lambda$  and  $h(\lambda)$  is given by

$$h(\lambda) = g(\lambda) - g(\lambda^{-1/2}) \quad (3)$$

Corresponding equations can be found for other homogeneous isochoric deformations (such as biaxial extension or pure shear) giving the forces in terms of the experimentally determined function  $g(\lambda)$ .

When  $N$ , the number of segments between intermolecular bonds per unit volume, does not change with time, Eq. (1) corresponds to a perfectly elastic material which will exhibit no stress relaxation. For elastomeric materials, this might be appropriate to describe equilibrium isothermal behavior at room temperature. That is, if we look at the behavior of an ordinary rubber at room temperature stretched from the undeformed state and held for a few minutes until the modulus settles down to the "rubbery plateau", the forces required to hold it stretched will then be almost constant in time and Eq. (1) will apply. The stress relaxation occurring at shorter times (sometimes called "physical" stress relaxation to distinguish it from "chemical" stress relaxation) is presumably caused by the slipping of intermolecular entanglements and other temporary bonds. The equilibrium stress of the "rubbery plateau", however, probably reflects chemical cross-links or other, more permanent bonds between segments. With time, in an aggressive atmosphere such as in geothermal down-well conditions, even these chemical crosslinks can be expected to break down and, as a result of the chemically active atmosphere new crosslinkages might be formed simultaneously. Suppose a sample of material is aged in such an atmosphere, then the quantity  $N$  of Eq. (1) will change in time reflecting the net change in crosslink density and giving rise to softening or embrittlement of the sample. Consider the following experiment. A virgin sample of elastomer with  $N_0$  effective segments between crosslinks per unit volume is extended to a stretch,  $\lambda$ , and the tensile force (when it settles down to a steady value) is measured. The sample is then allowed to recover and is then aged for a fixed time,  $t$ , in some atmosphere of interest. During this time the atmosphere will

cause crosslinks to break and to form or chain scission to occur so that  $N$  will change to a new value,  $N_0 + n(t) - m(t)$ , where  $n(t)$  is the number of segments formed in time  $t$  per unit volume and  $m(t)$  is the number of segments destroyed. At this point, the sample is removed from the aggressive atmosphere and the measurement of simple extension is repeated in the inactive laboratory atmosphere. If the  $\lambda$  and  $T$  apply for each simple extension measurement, Eq. (2) applies in each case with only  $f$  and  $N$  varying and we can write

$$f(t)/f_0 = (N_0 + n(t) - m(t))/N_0 \quad (4)$$

where  $f_0$  and  $N_0$  refer to the virgin sample and  $f(t)$ ,  $n(t)$ ,  $m(t)$  refer to the sample aged for time  $t$ . Thus, this experiment can be used to monitor the total change in segments per unit volume induced by the aging.

The present report covers experimental work consisting of the assembly of apparatus to simulate geothermal down-well conditions and some preliminary tests conducted on two samples of Y267 EPDM high temperature packer seal formulation (Y267-XXX11-6, and -7) which were supplied by L'Garde, Inc.

The environmental apparatus consists of a pressure vessel constructed from Hastelloy C-276. It was manufactured by LECO Corporation, Tem-Pres Division. It is rated for use up to 9000 psi at temperatures up to 400 °C. It provides a working chamber two inches in diameter and ten inches long. It can be placed in an electrical resistance furnace supplied by the same company together with a temperature controller. The pressure vessel is connected to a cylinder gas source with provisions for purging, bleeding, etc. The tubing and valves, etc. are all high pressure stainless steel construction rated up to 10,000 psi for atmosphere not hostile to type 303 stainless steel.

Test specimens were die cut from the 6 in. square sample. The specimens were straight strips 0.25 in. wide and 2.75 in. long. They were approximately 0.080 in. thick. They were held in small simple clamps each consisting of two small bars of aluminum between which the specimen could be held by means of two steel screws. The grips were designed so that specimens could be held at constant extension in a simple slotted cylinder device which would permit up to twelve specimens to be held in the pressure chamber simultaneously. The grips could also be attached simply to test fixtures which fit our hydraulic powered test machine.

This machine is controlled by a dedicated mini-computer. A BASIC language program was modified to perform a stress relaxation test in uniaxial extension. The samples were loaded into the machine and stretched 10 percent. The tension in the specimens was then measured at times between 0.05 second and 100 seconds after the loading. We were thus able to cover approximately two and one half decades on a logarithmic time scale and the stresses were calculated.

Four specimens of each of the EPDM elastomers mentioned above were prepared. Their stress relaxation behavior was measured. They were then stretched by various amounts from zero to thirty percent. They were placed in the pressure chamber in deionized water. The system was then purged with nitrogen at

2000 psi four times to remove oxygen. The heater was turned on and during the time (approximately one hour) that the system was heating to 265 °C the system was purged twice more. During these purges the water was permitted to boil. The system was held between 260 and 265 °C for approximately one hour and then allowed to cool to room temperature. All of the specimens had failed at the clamps. Those which were unstretched showed severe crack damage in the area of the clamps. This disappointing result is probably due to the large localized biaxial strains imposed by the clamping.

The specimens were then reclamped and again tested in stress relaxation tests at 10 percent strain. The form of the stress relaxation curves had not changed but the level of stress required to maintain the strain had reduced by approximately 15 percent. There was no significant correlation of this decrease with the level of stretch. This may only indicate that they all failed early in the test and that they all spent most of the time at zero stretch. It appears that it will be necessary to redesign the specimens to avoid the high strain concentrations at the clamps. This might be accomplished by the use of dog-bone shape specimens or by the use of ring shape specimens which could be die cut from sheets. This would avoid the nonuniformity problems which we experienced in working with o-ring samples.



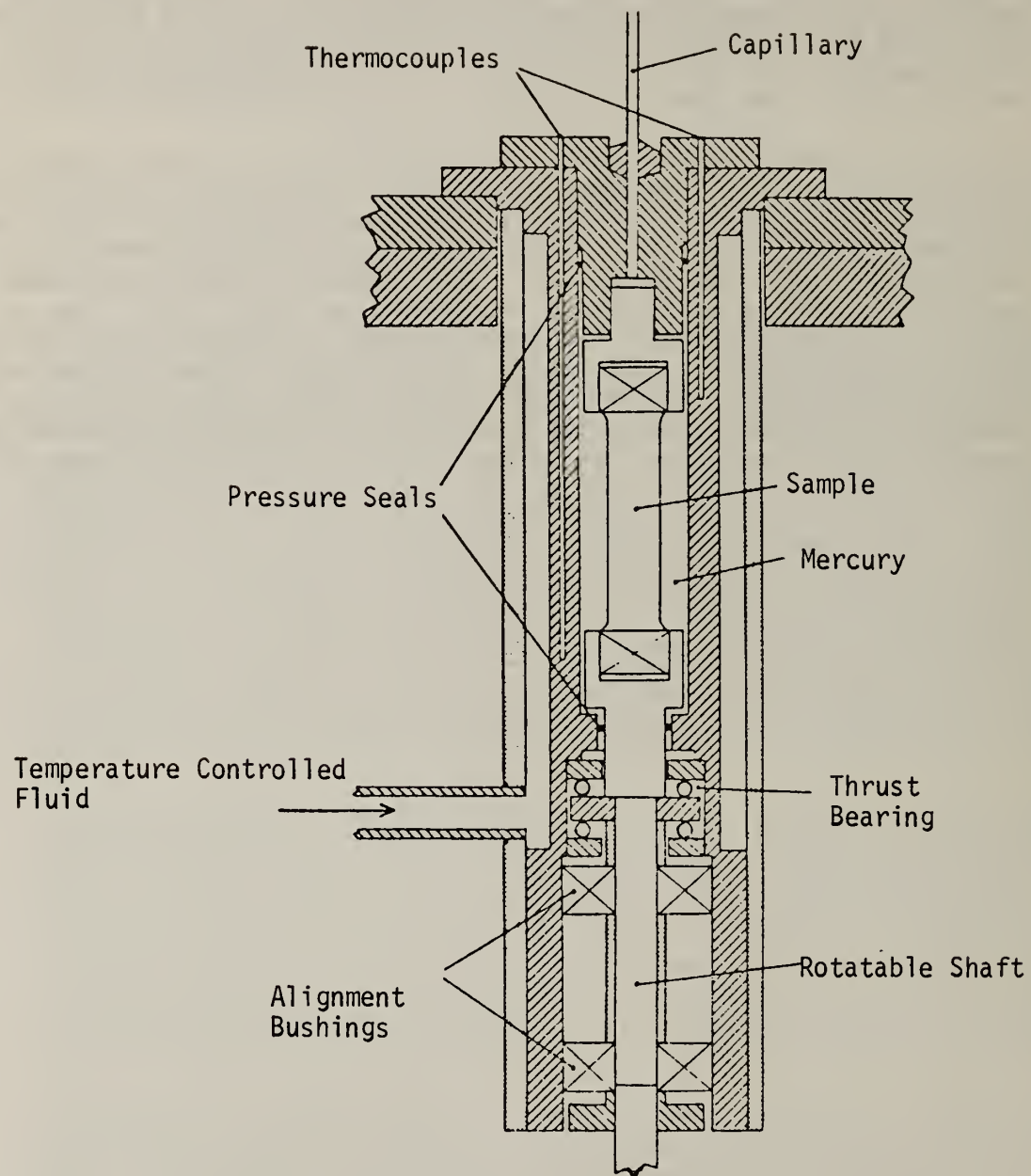


Figure 1 Schematic of the Torsional Dilatometer.

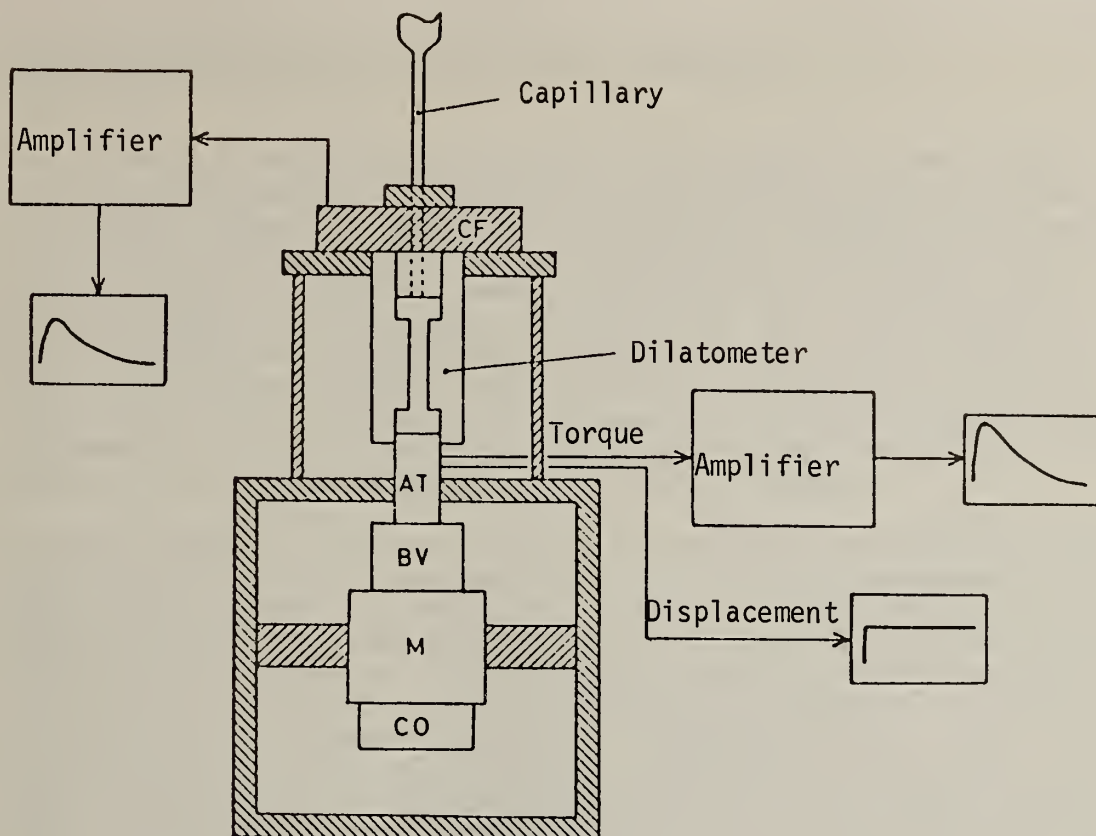


Figure 2 General schematic of the torsional dilatometer. CO = optical encoder, M = motor; BV = high precision gears; AT = drive shaft; CF = normal force transducer.

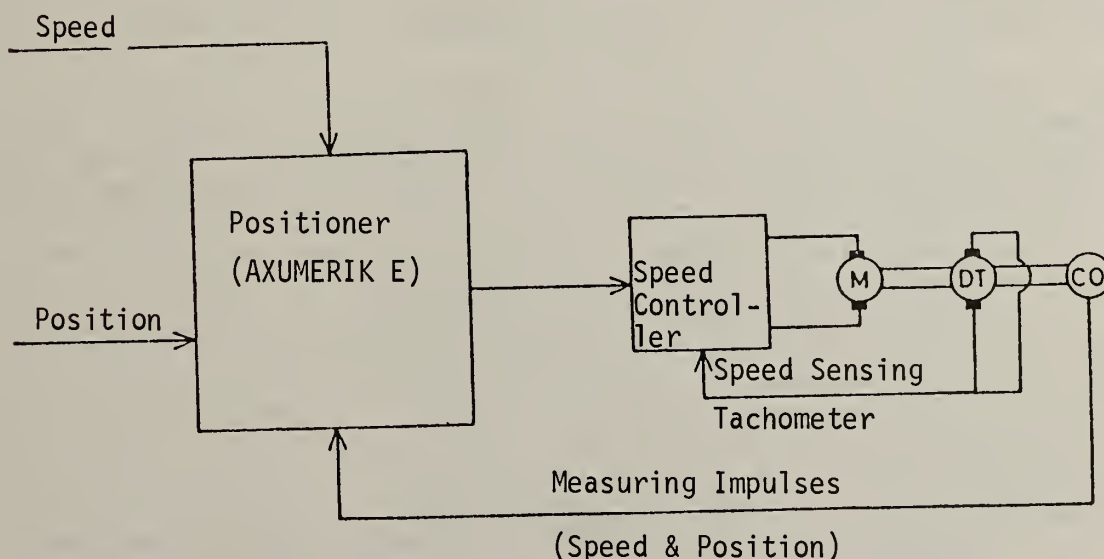


Figure 3 Schematic of servo-control system for torsional dilatometer. M = motor; DT = tachometer; CO = optical encoder. The Axumerik E represents the digital system which performs the calculations used to control the angular position.





PROCESSING AND RELIABILITY OF POLYMER COMPOSITES  
Task 12137

One of the most rapidly growing areas of high payoff polymer applications is composite materials. The addition of a reinforcement, as either particles or fibers, to polymers can dramatically improve their performance, and as a result they can be utilized in a wide range of generic applications where the requirements are beyond the capabilities of simple polymers. This expanded potential has led to increased usage in many diverse areas ranging from aerospace to automotive. Two major factors behind the expanding application of these materials are that their use is highly energy efficient and this can significantly reduce the need for critical materials such as cobalt and chromium whose limited supply is of critical concern to the national interest.

Although composite materials have great potential, the same multicomponent composition that is responsible for their high performance also gives rise to numerous problems with regard to the processing, fabrication, and prediction of failure behavior or service life. Since the composite field is still at an early stage of development, many of these problems can be directly attributed to a lack of basic knowledge, and adequate test methods in the composites area. In response to this need, a new Task has been initiated during 1982. The objectives are to carry out long range research to provide industry and other Government agencies with test methods, material property data and failure prediction models that are essential if the full potential of these materials is to be achieved. In line with the two primary problem areas mentioned above, there are two major thrusts in this Task. The first seeks to gain a better understanding of the basic science involved in processing and fabrication of these materials while the second addresses the development of the basic science concepts, methods, and data needed to assist in improving durability and enhancing the capability for failure predictions.

During the first year Task programs have been developed to address both areas of concern. Several projects are studying cure, i.e. the chemical reactions that occur during processing and represent the most important factor in successful fabrication. Of special interest are experiments investigating rapid cure and the curing of films since these areas are of great practical importance. Another program is developing quality control techniques for raw materials, an area of great concern to industry. The failure behavior of both particle and fiber reinforced polymers is also being studied with special emphasis on the development of techniques, such as X-ray scattering, which can provide information about the state of the materials prior to fracture. To assist in conducting this broadly based effort three outside experts spent time working in the Division during the last year: Dr. Raganathan, an industrial research associate from Martin Marietta; Dr. James Koutsky, an Intergovernmental Personnel Act employee from the University of Illinois; and Dr. Anthony Kinloch, a foreign guest worker from the Ministry of Defense in England.

Failure Behavior of Particle Reinforced Polymer Composites  
Subtask 1 of Task 12137

D. L. Hunston, A. J. Kinloch, and G. W. Bullman

Most of the polymers used in structural application are inherently brittle and must be reinforced or toughened. One empirically developed method that has proven to be quite successful is the incorporation of small particles of a softer material in a matrix of the brittle polymer. Although composite materials of this type often have very high fracture energies their failure behavior is usually quite complex and involves large viscoelastic effects.

In an effort to gain a fundamental understanding of the failure behavior of such materials, NBS is currently studying two different model systems: a polysulfone filled with polytetrafluoroethylene particles and an epoxy with epoxy/polybutadiene particles. The first system is of interest to the Navy for certain seal applications while the second serves as a model for most commercial structural adhesives. The program focusses on developing test methods for such materials and studying the mechanisms of failure. As part of this effort a joint program was initiated in 1979 with scientists from the University of Illinois and the Ministry of Defense (Waltham Abbey Laboratory) in England<sup>1-4</sup>. During the last year, Dr. A. J. Kinloch from Waltham Abbey spent 3 weeks at NBS as a guest worker to help coordinate results from various parts of the program. As a result of this visit the empirical failure model developed two years ago in this program has now been extended to 4 different elastomer-modified epoxy formulations. The most significant aspect of this development is that the temperature dependence for all 4 systems could be described with a single Arrhenius type activation energy whose value was identical to that obtained from yield experiments. It has previously been suggested that yielding was a crucial step in the toughening mechanism for these materials but this provides the first direct evidence for a relationship between the two properties.

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- [2] Bitner, J. L.; Rushford, J. L.; Rose, W. S.; Hunston, D. L.; Riew, C. K. J. Adhesion 13: 3; 1981.
- [3] Kinloch, A. J.; Shaw, S. J.; Hunston, D. L. Proceedings of the International Conference on Deformation and Fracture. Cambridge, England, 1982, March.
- [4] Hunston, D. L.; Wang, S. S.; Kinloch, A. J. Organic Coatings and Plastic Preprints 47: 407; 1982.



Interlaminar Fracture of Composites  
Subtask 2 of Task 12137

D. L. Hunston, G. W. Bullman, and J. A. Koutsky

A major area of concern in the use of continuous-fiber reinforced composites is delamination, that is the growth of cracks between the layers of fibers. Delamination can substantially reduce the performance of composites in numerous ways but compression strength is particularly sensitive to this type of damage. The conventional polymeric matrix resins, i.e., the material that binds the fiber together, are very brittle and therefore subject to damage particularly when loaded by impact. This damage involves matrix cracks which can easily grow into large areas of delamination. The problems this can generate in practical applications have led to a widespread interest in developing polymeric matrix materials with improved resistance to both initial damage and subsequent growth of this damage into a delamination. In addition, there is a need to develop design data that can be used to predict the growth rate of a delamination. Unfortunately, although a number of test methods are now being used, few if any have been developed to the extent that they can provide the quantitative information that is needed.

In response to this problem, a joint program has been established among researchers at NBS, NASA Langley, the University of Illinois, and several composites manufacturers. As part of this program, NBS is examining various test methods for determining interlaminar fracture. The tests employ specimens with either rectangular or triangular geometries. A precrack is generated between fiber layers in the specimen and an increasing load is applied perpendicular to the precrack so that subsequent crack growth occurs between the layers of fibers. The critical value at which this crack growth begins is noted and converted to a fracture energy using appropriate equations.

During the last year, the program has studied the effects of specimen size, geometry, and lay-up (the sequence of fiber layers and their orientations). Data from these tests have been correlated with the stress analysis work at the University of Illinois and the composites testing program at NASA Langley. These results have led to a series of guidelines for the design of test specimens when the polymeric matrix is a brittle material. Future work will focus on testing composites made with toughened matrix materials and thermoplastic resins. The effects of loading rate, temperature, and environment on the fracture test will also be examined. This will help establish both the validity of the test methodology and a data base of information for model systems representing the various types of polymers.



A Non-Destructive Technique to Monitor Cure of Adhesive and Composite Resins

Subtask 3 of Task 12137

D. L. Hunston and J. A. Koutsky

In applications such as fiber-reinforced composites and adhesives the polymer must be fluid in the early stages of fabrication so that the proper flow, leveling, wetting and spreading at interfaces, etc. can be achieved. The polymer must then harden by cooling, solvent loss, or chemical reactions to form a rigid material. In most cases the successful fabrication of a final product requires that associated changes in mechanical properties take place at the appropriate times and rates. It is desirable therefore to have nondestructive techniques that can monitor these changes as they occur. Unfortunately, this is generally very difficult, particularly since many of the applications involve thin films, whose mechanical properties are difficult to measure and cannot usually be predicted from experiments on bulk samples.

To address this problem, an effort is being made to develop a new method for nondestructively characterizing thin films. During the last year an ultrasonic shear wave technique has been studied as a candidate test method. The experiment involves the propagation of a shear wave in a quartz plate coated with the thin polymer sample. By monitoring the attenuation of the wave in the strip, it is possible to follow changes that occur in the coating. The first samples tested were an epoxy-type polymer that cures by free radical initiation. Figure 1 shows a plot of attenuation vs curing time for two formulations containing the same epoxy but with different concentrations of accelerator. The experiments clearly show that there is an initiation period prior to the onset of cure. The rate of cure influences the width of the transition while the ultimate attenuation level depends on the structure of the cured film among other factors. When the accelerator concentration is changed both the reaction rate and the induction period are altered but the ultimate attenuation level remains the same. This type of information can be crucial in designing epoxy-based adhesives and composites.

The results to date indicate that this technique can be used to qualitatively monitor changes that occur during the liquid-to-solid transition in important polymer systems. During the next year an effort will be made to quantify this test. As part of this effort the measurement capability will be expanded to permit the determination of velocity as well as attenuation. In addition, the program will investigate the possibilities for coupling this technique with other methods such as dielectric tests that may be more amenable to process control measurements. The information provided by this coupling would make both measurement techniques more useful.

Measurement of Microvoids and Microcracks in Composite Materials Using  
Small Angle X-ray Scattering Techniques  
Subtask 4 of Task 12137

W. L. Wu

Small angle x-ray scattering (SAXS) has been used extensively in structural characterizations of heterogeneous systems. Most work, both theoretical and experimental, deals with systems composed of only two phases. A theoretical development treating systems of three phases (matrix, reinforcing fibers or fillers, and microcracks) has been advanced. It is shown that the volume content and the characteristic lengths of the microcracks or voids can be determined from the angular dependence of the x-ray scattering intensities. The analysis are valid for both deformed and undeformed specimens. Incorporating the experimental data, useful information regarding the size and content of microcracks within damaged particulate composites has been obtained.

Industrial Research Associate Program on Thermal and Spectroscopic  
Properties of Polymer-Based Composite Materials  
Subtask 5 of Task 12137

B. N. Ranganathan, J. H. Flynn, and B. M. Fanconi

Dr. Ranganathan (Martin Marietta Corporation) completed a six-month Research Program in the Polymer Science and Standards Division. During this time, extensive use was made of NBS equipment to evaluate potential test methods as a basis for the establishment of quality control procedures which promise to significantly reduce the cost of inspecting the Thermal Protection System (TPS) which insulates the External Fuel Tank for the Space Shuttle.

The TPS insulation consists of a superlight ablator composite material, approximately 1/2 in. thick, that is applied directly onto the outer surface of the aluminum external tank, and, on top of the composite ablator material, approximately 3/4 in. thick polyurethane foam is applied for additional insulation. TPS insulation serves an important function in that it prevents ice formation, and also minimizes boil-off of the cryogenic liquid fuels.

The composite superlight ablator layer of the thermal protection system is functionally more critical than the polyurethane layer. The composite consists of silicone resin, glass fibers, carbon black, phenolic microspheres, silica microspheres, cork, etc., of which silicone resin is the most important component for it serves as the binder that holds together all the other components of the composite, and further functions as an adhesive that bonds the composite to the aluminum surface of the external fuel tank.

The present investigation is concerned with the evaluation of silicone resins. The main purpose of this research was to develop effective quality control procedures using state-of-the-art techniques that are rapid, accurate, and more reliable than the currently used methods, so that a "good" lot can be distinguished from a "bad" lot of material.



This distinction of a "good" from a "bad" material is of immense importance, as it alleviates expensive repairs that are labor intensive, and results in a very cost effective external tank program.

Two types of silicone materials were evaluated as a part of this investigation. Both types are purchased commercially, and as such the exact chemical formulations are proprietary in nature. Type I silicone is fast curing (gel time--10 mins) and low strength (tensile strength approximately 50 psi), while Type II is slow curing (gel time--several hours) and high strength (tensile strength approximately 1000 psi); the higher strength of the latter is due to the presence of a filler material. Both types of silicones are two component systems, and the curing mechanism is via an addition reaction between silane (component-B) and vinyl (component-A) groups; in addition, component A contains a platinum catalyst. In manufacturing, an A to B ratio of 10:1 is used.

Two techniques; namely, DSC and FTIR, were evaluated for their viability as effective quality control procedures for the intended purpose. Evaluation of individual components was not possible using DSC; that is, no useful thermal property information was obtainable in the temperature range of interest. Therefore, DSC was used solely for studying the curing reaction. On the other hand, FTIR permitted the evaluation of individual components as well as the curing reaction.

Results obtained to date indicate that FTIR is a viable quality control technique. An attempt will be made to use this technique in the future at the Martin Marietta quality control laboratory for the evaluation of polymeric raw materials prior to their use in manufacturing.

The establishment of FTIR as a viable quality control technique with its intended future application and attendant benefits at Martin Marietta Aerospace is a direct result of the research associate's work at NBS.

#### Analysis of Rapid Thermoset Resin Curing Subtask 6 of Task 12137

G. A. Senich

Thermosetting resins are distinguished from the thermoplastics by the three-dimensional nature of the chemical linkages formed in these materials during the cure process. A network of chemical bonds is formed irreversibly by heat or chemical means during curing or cross-linking processes and renders the material substantially infusible and insoluble. This is in contrast to thermoplastic materials which are capable of being repeatedly softened when heated and hardened when cooled. Articles fabricated from thermoset materials are generally insoluble, resistant to dimensional changes and flow, and able to withstand high temperature heating without melting.

Thermosets are considerable articles of commerce. Their usage in the U.S. has been estimated to amount to over 1.1 billion pounds in 1979. The most commercially important thermosetting resins are phenolic-, urea-, and melamine-formaldehydes, alkyds, polyurethanes, epoxies, and polyesters. These materials are commonly used as the polymeric matrix



of highly filled structural composites, a market which amounted to over 2 billion pounds of fabricated material in the U.S. for 1979. Composite parts are produced by molding or laminating operations which generally require either a long time in a closed mold or press at a high temperature and pressure or a lengthy post-cure outside the mold, again at high temperatures. These long times for thermal curing, on the order of one to several hours, restrict the rate of production of composite articles. Rapidly curing thermoset resins could greatly reduce production time and permit a large increase in the volume of fabricated composite output.

Another area in which rapid curing is of preponderant importance is the printing process. At typical paper speeds, a thermoset polymeric ink has only a one to ten second curing period for achieving sufficient mechanical strength to allow the substrate to be wound onto a takeup roll without damage to the printed image. Natural-product based inks are now used in intaglio currency printing operations and usually provide acceptable performance. However, it is desirable to investigate rapidly curing synthetic thermosetting resins that could alleviate some of the difficulties encountered with material variability and undesirable solvents in printing with the current inks as well as others anticipated to occur with the introduction of new printing machinery.

A program has been initiated to assess the current state of rapid-cure thermoset matrix resin science and technology. Suitable example systems of interest, principally epoxies, acrylated oligomers, and unsaturated polyesters/acrylics, are being examined. Test methods for chemical or functional group characterization by FTIR, and mechanical characterization by rheometer and viscometer are being developed and coordinated to provide an understanding of how chemical reactivity and mechanical properties are related during the curing process. Novel methods for studying the kinetics of rapid curing, such as monitoring the mechanical property changes of a thin, curing film on a quartz substrate by ultrasonic shear wave propagation, are also being employed. The program will provide a better understanding of the chemistry of processing thermoset polymers and aid in the identification of possible candidate materials for special applications, such as rapidly curing synthetic thermosets suitable for use as ink vehicles, matrix resins which could increase the rate of production in the manufacture of composite articles, and repair formulations for quick mending of composite parts.

#### Degree of Polymerization of Thermoset Resins Used in Composites Subtask 7 of Task 12137

W. L. Wu and B. M. Fanconi

Physical properties as well as the resistance to adverse environments of thermoset resins depend strongly on the degree of polymerization (state of cure). The curing process of thermoset resins is believed to be incomplete if the curing temperature is well below the glass transition temperature ( $T_g^\infty$ ) of the polymers in their completely cured states. This situation is commonly encountered in practical cases.

A FTIR technique was developed for monitoring the degree of cure and was applied to assess the degree of polymerization of commonly used thermoset resin systems. Cure characteristics were examined as a function of type and amount of initiators and accelerators, as well as the flexibility of the prepolymer. It has been found that only a limited amount of polymerization occurred after the vitrification points. The degree of polymerization is mainly controlled by the viscosity of the monomer instead of the type or amount of the initiators.

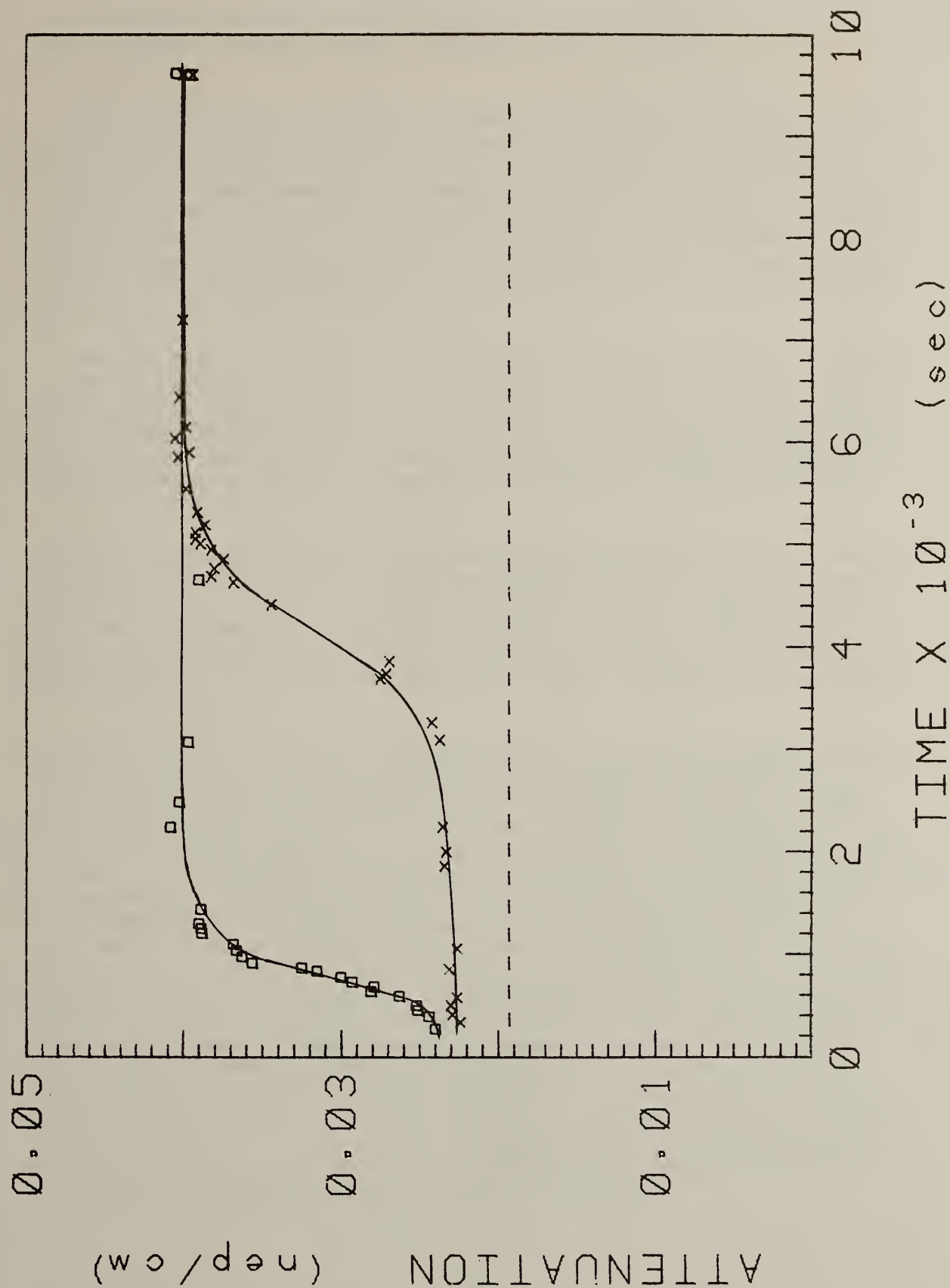
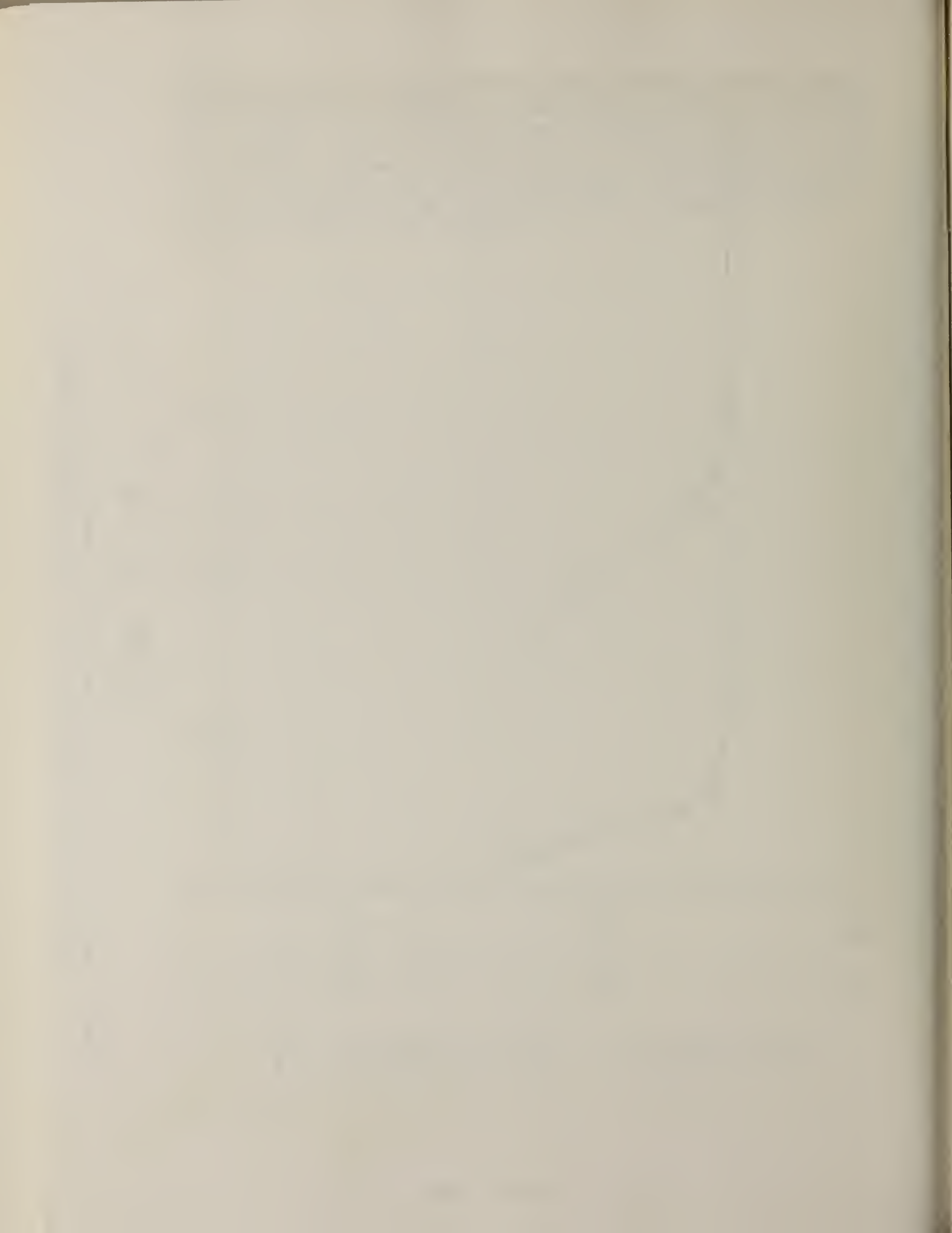


Figure 1 Cure data for the epoxy/accelerator system, dashed line for uncoated strip, x for 0.25 percent accelerator, and x for 0.35 percent accelerator.





## ADDITIVE MIGRATION AND CHEMICAL DURABILITY OF POLYMERS

### Task 12138

Polymeric materials find many high payoff applications in construction, transportation, and electrical systems where long-term durability is essential to competitive performance. The growing use of polymeric materials in these generic applications, generates a need for long-term research aimed at providing a scientific basis for accelerated tests of service life. In fact, a recent report by the National Research Council states, "The lack of adequate measurement techniques for predicting the service life of new materials and components is a major barrier to the acceptance of polymeric materials."

To develop reliable methods for predicting the service life of polymeric materials, we need to identify the scientific basis of (1) the rates and mechanisms by which polymeric materials degrade under the appropriate environmental conditions and (2) the rates and extents of the migration of protective additives from polymeric materials. The collection and interpretation of these two types of information have been the main effort in this task.

Research this year on degradation mechanisms and rates includes investigations of the hydrolysis of polyesters and the use of thermo-gravimetry to measure the rates and activation energies of the thermal degradation of several polymers. In addition, we have initiated a collaborative program with the Building Materials Division to investigate the kinetics and mechanism of the photodegradation of PMMA, a polymer widely used for solar cover plates.

Almost all useful polymeric materials have low-molecular-weight substances incorporated in them to develop or maintain desirable properties. In use, these substances inevitably diffuse through the polymer to some extent and may migrate out of the polymer entirely. The polymer is then left with poorer properties or made more vulnerable to degradation and failure. This is a major failure mode of polymers, and lifetime prediction methods must explicitly include the rates of additive diffusion along with the rates of the inhibited and uninhibited degradation reactions. The number of commercially usable polymer-additive combinations is too large to be considered efficiently on a case-by-case basis. The emphasis in this task is, therefore, on the development of general principles or models of diffusion that are applicable to the widest range of generically important systems. In addition, knowledge of the general principles which control diffusion through solid polymers is important to the design and evaluation of improved additive systems. Work this year on the migration of additives includes measurements of diffusion rates by solvent extraction and by inverse chromatography and investigations of slow diffusion in solid polymers and concentrated polymer solutions by microfluorimetry and by a photobleaching technique.

Hydrolytic Degradation of Polyester Polyurethane Elastomers  
Subtask 1 of Task 12138

D. W. Brown, R. E. Lowry, and L. E. Smith

Polyester polyurethane elastomers are useful specialty polymers. Unfortunately, their ester linkages are subject to acid-catalyzed hydrolysis. Earlier, we investigated this process and developed kinetic schemes that can be used to predict lifetimes of these polymers, with and without carbodiimide stabilizers.

In this year we investigated several additional aspects of this hydrolytic degradation.

Published data indicate that cross-linked polyester polyurethanes in magnetic tape binder may appear stable to hydrolysis at about 25 percent relative humidity, RH, because of the equilibrium between ester hydrolysis and esterification [1]. This equilibrium ought to be general for ester hydrolysis and so may affect estimates of hydrolytic stability in other polyester systems. We determined the equilibrium acid contents,  $[A_e]$ , in three polyester diols and in soluble poly(butylene adipate) and poly(caprolactone)-based polyurethanes. Values of  $[A_e]^{-1}$  are about  $7 \times 10^{-4}$  mol/g at 25 percent RH. Molecular weight of the polyurethanes equals  $[A_e]^{-1}$ , about 1400, if there is one acid group per molecule. The equilibrated polymers are weak, brittle, solids. Presumably the initial crosslinks or perhaps reaction of acid with iron oxide made the polyurethane appear more stable on the equilibrated tape.

Another study concerned the behavior of carbodiimide stabilizers. We had observed that polyester polyurethanes consumed carbodiimide stabilizers from three to ten times faster during hydrolytic aging than did the polyester diols used to make the polymers. We made a poly(caprolactone) diurethane diol from a 2:1 mixture of diol and diisocyanate. This material consumed carbodiimide during hydrolytic aging about as slowly as the polycaprolactone diol. Thus, the difference in rates of carbodiimide consumption was not explained but is not associated with the presence of urethane in the polymer.

A third study was made of the effect of the initial acid content on the rate of consumption of carbodiimide. We used the same number of moles excess carbodiimide over acid in two polybutylene adipate diols that differed in initial acid contents by a factor of 20. The diol having the higher initial acid content consumed the excess carbodiimide faster during hydrolytic aging. Presumably this was due to hydrolysis of the acyl area produced by reaction of acid and carbodiimide. At lower initial acid contents this reaction apparently is not important because uncatalyzed hydrolysis of ester also consumes carbodiimide. The result indicates the practical importance of using low acid diols in making polyurethanes, even if a stabilizer is to be used.

[1] Cuddihy, E. F. IEEE Trans. Mag. 16: 558; 1980.



Prediction of the Long-Term Stability of Polyester-Based Recording Media  
Subtask 2 of Task 12138

D. W. Brown, R. E. Lowry, and L. E. Smith

PET is the base material in many information storage and retrieval systems. We are investigating methods of estimating the useful lifetime of PET in archival storage, under sponsorship of the National Archives. Hydrolysis of the ester linkage is the most important cause of degradation. Various samples are being aged under a variety of conditions. Samples have been examined after aging at 55, 85, 100, and 115 °C at 25 to 100 percent RH. Gel permeation chromatograms were used to calculate molecular weights. They indicate that about one scission/ original molecule ( $5 \times 10^{-5}$  mol scission/g polymer) makes the polymer quite brittle. The imprecision in molecular weight is such that scissions probably are uncertain by  $1$  to  $2 \times 10^{-5}$  mol/g. Thus, the gel chromatograph, which consumes only about 5 mg of PET per determination, does not appear to measure chain scissions with enough precision to anticipate embrittlement. Efforts will be made to improve the precision of this measurement.

Acid contents were measured by potentiometric titration. The change in acid content is about equal to the number of scissions, as is expected for hydrolysis of a polyester. Acid contents are somewhat more precisely known than molecular weights but measurement of the former requires about 2 g of polymer. This is too much for use as a monitoring technique.

Attempts will be made to develop infrared and sonic methods of analysis.

Examination of Processes in Thermogravimetry  
Subtask 3 of Task 12138

B. Dickens

Calculated vapor pressures have been used [1] in a first-approximation model of the vapor above thermally degrading polyethylene [2]. The results suggest that the "normal boiling" of large molecules in the range  $C_{30}$  to  $> C_{90}$  forces the rapid growth of bubbles in polyethylene degrading at low pressures, and the bubbles grow to significant size because the liquid is relatively elastic. The trend of decreasing apparent overall activation energy with increasing pressure is ascribed to contributions of low latent heats of vaporization from molecules up to  $\sim C_{30}$ , depending on the imposed pressure. The trends of vapor composition for various temperatures and pressures have been studied. In general, both the temperature and the pressure should be as low as possible to minimize the contribution of the latent heats of vaporization to the overall activation energy and interference from bubbles in the molten degrading polymer.

Table 1 gives the activation energies found [2] for thermally degrading polyethylene, together with the associated pressures, temperatures, and apparent orders of reaction (calculated over small changes in extent of reaction,  $\sim 5$  percent, at extents of reaction greater than 40 percent). The activation energies were determined using the factor-jump method of

thermogravimetry, which avoids the need to specify a form for the dependence of the rate of weight loss on the extent of reaction and also determines the activation of energy without any correlation with the preexponential factor of the Arrhenius equation. Such activation energies are expected to be relatively unbiased.

Table 1  
Effect of Pressure on Kinetic Parameters of Thermally  
Degrading Polyethylene

	pressure, mm Hg of N <sub>2</sub> + volatiles		
	~ 0.005	8	800
E (kcal/mole)	65.4 ± 0.5	64.8 ± 0.3	62.6 ± 0.5
temperature <sup>a</sup> , °C	425	445	460
bubbles?	yes	no	no
order of reaction	1.5 ± 0.5	0.8 ± 0.3	0.7 ± 0.3

<sup>a</sup>For roughly equal rates of weight loss from approximately the same size of sample at roughly the same extent of degradation at the specified pressure.

The apparent overall activation energy and the apparent order of reaction decrease as the pressure increases (table 1), which suggests that simple evaporation [3] is a significant factor. Evaporation of liquid alkanes such as C<sub>36</sub>H<sub>74</sub> is easily shown experimentally to be of zero order, depending only on the available surface area, when the vapor pressure of the pure liquid is below the external pressure. When the vapor pressure is equal to the external pressure, normal boiling occurs in that the temperature of the liquid depends on the applied pressure and ideally cannot be increased by increasing the heating rate. Such increases provide more vapor, and when the quiescent surface area is not sufficient to allow the required amount of vapor to form, more surface area is provided through the creation of bubbles.

In vacuum conditions, unsteadiness in the sample weight is observed and has been attributed to bursting bubbles. No shocks to the balance are observed at overall pressures of 8 and 800 mm Hg of N<sub>2</sub>. The calculations show that normal boiling ceases at ~ C<sub>29</sub> for 8 mm Hg and 445 °C, at ~ C<sub>8</sub> for 800 mm Hg and 460 °C, and at ~ C<sub>85</sub> for 0.005 mm Hg and 425 °C (see table 1) for the hypothetical mixture of hydrocarbons. Thus the vacuum case requires that molecules up to C<sub>85</sub> be forced rapidly out of the liquid. The slowness of diffusion for the largest of these molecules (C<sub>30</sub> to C<sub>85</sub> were not under boiling conditions at 8 mm Hg and 445 °C) to the quiescent surface must require the formation of "local surface" in the form of bubbles, so that they may be volatilized. Because most nucleation is heterogeneous, these bubbles would form on the wall of the sample cup. The smaller molecules will have very large vapor pressures at the temperatures of interest and are so unstable with respect to



boiling that they are able to enter even very small bubbles. Thus the small molecules will act as a dissolved permanent gas. In this sense, the smaller molecules "nucleate" the bubbles which then accept the larger molecules as the bubble size increases.

The temperatures in table 1 correspond to degradation rates of  $\sim 1:4:10$  when the observed [1] activation energy of 65.4 kcal/mole is applied. These temperatures are for approximately equivalent rates of weight-loss under the pressures specified in table 1. Since the weight loss is independent of whether methylene units are joined or not, this means that, for equal overall rates of weight loss, samples which are degrading faster because of their higher temperature are volatilizing shorter molecules. In particular, the average molecular weights in the vapor phase are  $1:1/4:1/10 = 1:0.25:0.1$  at these temperatures.

The calculated average number of carbon atoms per volatilizing molecule is 49:20:9 for the three cases considered. These values lie in the ratio 1:0.41:0.18. The last two are in approximately the correct ratio to each other. The first, for the near vacuum case, is somewhat too low, as expected because the tail obviously should include molecules longer than  $C_{100}$ , but these molecules were not included in the calculations because their Antoine coefficients are not available. Also, the total pressure was probably not exactly the 0.005 mm Hg assumed for the vacuum case and the upper limit of boiling molecules is very sensitive to the total pressure in this region. A lower pressure would give a higher average molecular weight and a greater range of boiling molecules.

The important aspect is to minimize the tail representing "normal evaporation" as opposed to "normal boiling", and the calculations show that the appropriate conditions are that the pressure should be as low as possible. The temperature has less effect in reducing the proportion of weight loss by evaporation but has a large effect on the size of molecules volatilized and hence on the propensity for explosive bubble formation. The results also indicate the extent to which the assumption of a sharp cut-off in the size of molecules volatilized is realistic. The largest molecule evaporating during degradation in vacuum was assumed to have  $\sim 70$  carbon atoms in the Wall-Simha treatment [4,5]. Suehiro and O'Shima [6] estimated an upper limit of  $\sim 26$  carbon atoms for evaporation in an inert atmosphere at 420 °C. This upper limit is indeed dependent on the imposed pressure and is really a distribution. The cut-off is sharpest at very low pressures, and changes markedly with temperature. Also, as Wall et al. remarked [4], it may be expected to vary with extent of degradation. The dependence on temperature and degradation probably explains much of the discrepancy in degradation products reported for polyethylene.

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Thermogravimetric Studies of Polymer Degradation  
Subtask 4 of Task 12138

B. Dickens

Thermogravimetry is often and widely used to study polymers because it can be applied to specimens in any condensed form. In a continuing series of investigations, we have used the highly automated factor-jump method of thermogravimetry, developed at NBS, to study the thermal degradation of polyisobutylene (PIBu).

The overall activation energy,  $E_a$ , of the thermal degradation of PIBu has been measured to be  $49.2 \pm 0.3$  kcal/mole ( $207 \pm 1$  kJ/mole) over the range 365 to 405 °C in  $N_2$  at 800 mm Hg pressure and flowing at 4 mm/s over the sample. This is consistent with some values reported for thermal degradation in vacuum and in solution. In 5 mm Hg, an apparent activation energy of  $52.1 \pm 0.5$  kcal/mole ( $218 \pm 2$  kJ/mole) was found and, in vacuum, a value of  $57 \pm 3$  kcal/mole ( $238 \pm 13$  kJ/mole). Troublesome bubbling made the vacuum values difficult to measure.

Substitution of reasonable values for the activation energies of initiation,  $E_i$ , and termination,  $E_t$ , and the activation energy,  $E_a$ , for vacuum degradation in the equation  $E_a = E_i/2 + E_d + E_t/2$ , yields an activation energy  $E_d = 20$  kcal/mole for the unzipping reaction. This equation presupposes a degradation mechanism of random initiation, unzipping, and bimolecular termination. Substitution of reasonable values of  $\Delta H$ , the heat of polymerization, in the definition  $\Delta E = E_p - E_d$  suggests that the activation energy of polymerization reaction at 375 °C is approximately 7 kcal/mole.

Variable Heating Rate Thermogravimetry  
Subtask 5 of Task 12138

J. H. Flynn

The prediction of the lifetime of a polymer by extrapolation from weight-loss data requires a thorough analysis of the degradation kinetics both in the initial phases and over a wide temperature range. Techniques have been developed in which entire kinetic spectra are compared among experiments performed at heating rates from 6 °/min to 9 °/day. Simple methods of plotting data from these techniques have been used for diagnosing shifts in reaction mechanism, uncoupling of competing processes, and testing the validity of kinetic models.

Considerable weight-loss in vacuum, nitrogen, or air is found to occur below 200 °C when toluene-2,4-diisocyanate (TDI) and diphenyl methane-4,4'-diisocyanate (MDI), polyether and polyester soft segment, 1,4-butanediol polyurethanes are heated at very slow rates. Weight-loss

in vacuum is punctuated with bursts of volatiles as the internal pressure of the dissociated diisocyanate builds up more rapidly than it can dissipate by diffusion. TDI polyurethanes degrade at lower temperatures and with lower activation energies than do MDI polymers due to their faster diffusivity and greater volatility. These factors suggest that techniques may be developed for the direct recovery and reuse of diisocyanates from polyurethane wastes.

Photolytic and Thermal Degradation of Poly(Methyl Methacrylate)  
Subtask 6 of Task 12138

B. Dickens

A study on degradation in solar cover plate materials is being carried out in collaboration with D. Waksman and J. W. Martin of the NBS Center for Building Technology. PMMA was selected as an appropriate material because it is inexpensive, relatively resistant to weathering, and noncrystalline (and therefore has no complications from preferred orientation). Approximately 1 in. square specimens of 1/16 in. thick plates of UV-absorber free PMMA were exposed to five different temperatures and four levels of xenon arc radiation filtered through borosilicate glass. Nearly all published studies on photodegradation of PMMA used 254 nm radiation, which is readily absorbed by the ester groups of PMMA. This study used only wavelengths greater than 300 nm to simulate degradation by solar radiation.

Mechanical properties are well known to be influenced by changes in molecular weight. In particular, reduction in the molecular weight of PMMA causes embrittlement (once a critical level is reached) and lowering of the glass transition temperature. Molecular weight distributions were therefore determined for more than 250 specimens (including triplicates and controls) using gel permeation chromatography. Computer programs which allow data collection and data processing with considerable precision were written by J. D. Barnes and F. L. McCrackin of the Polymer Science and Standards Division.

In addition to analysing the effect of the degradation on the whole specimen, we measured the molecular weight distribution as a function of depth along the irradiation direction. Microtoming was unsatisfactory because the material was too brittle. Milling was a satisfactory way of providing more than 20 slices, provided the specimen was large enough. Because of the small size of most specimens, we first sawed selected specimens into up to 5 slices with a diamond wafer saw. GPC analysis of these slices has shown approximately equal degradation on the front and back sides of the PMMA sheets and considerably less in the center, probably due to oxygen starvation there. Quantitative analysis of chain scissions in terms of degradation temperature and incident flux is now beginning.

UV spectra are being used to investigate chromophores which are formed and consumed during the degradation. Shifts in the edges of the UV absorption bands in PMMA are being studied using difference spectra on whole and on sliced specimens. The bands appear to correlate with the extents of thermal and photolytic degradation.



Water analysis using FTIR to study the  $5263\text{ cm}^{-1}$  IR absorption of a water combination band has shown that PMMA is extremely sensitive to the humidity of the atmosphere and typically contains 1 to 2 percent water. The effects of such levels of water on the degradation mechanism through plasticization of the PMMA will be studied next.

#### Fluorescence Measurement of Antioxidant Migration from Low Density Polyethylene into 1-Propanol

Subtask 7 of Task 12138

F. W. Wang and B. F. Howell

Although the fluorescence technique has been used to determine additive concentrations in polymers [1,2], to our knowledge, there has been no report on the use of this technique to measure the diffusion of an additive from a polymer matrix into an extracting solvent. To carry out successfully a diffusion measurement by the fluorescence technique, one must take precautions to exclude oxygen from the extracting solvent since oxygen quenches the fluorescence of the additive and, in some cases, contributes to its photodegradation. We describe here how oxygen exclusion was incorporated into a procedure to measure the diffusion of an additive from a polymer matrix into an extracting solvent. We also describe the application of this procedure to the diffusion of an amine antioxidant, N,N'-diphenyl-p-phenylene-diamine (DPPD), from low-density polyethylene (LDPE) into 1-propanol and we give a preliminary value for the diffusion coefficient of DPPD in LDPE under the experimental conditions described below.

#### Experimental

##### DPPD-LDPE Films

DPPD was purified by recrystallization from toluene. NBS-SRM 1476, a low-density polyethylene whole polymer, was washed under a nitrogen atmosphere, first with toluene at  $110\text{ }^{\circ}\text{C}$ , and then with heptane at  $22\text{ }^{\circ}\text{C}$ . The DPPD-LDPE powder, in which 0.05 wt. % of DPPD was uniformly distributed, was pressed in air into pellets with an IR pellet press. These pellets were placed in teflon molds, fused under a nitrogen atmosphere, and then quenched with dry ice. The films thus obtained were approximately 0.355 mm thick; they were trimmed with an arch punch to form discs 0.95 cm in diameter. Two films were a combined mass of  $0.49 \pm 0.006\text{ g}$  were extracted during each diffusion coefficient determination.

##### Extraction Procedure

Ten ml of 1-propanol were added to a weighed, specially constructed extraction vessel (fig. 1). A side arm of the vessel (A in fig. 1) was attached with wax to a high vacuum line. Solvent in chamber D was degassed inside the vessel by repeated freezing, evacuation and thawing. Partial loosening of the stopcock (E in fig. 1) opened the vessel to the vacuum line while sealing it from the atmosphere. By means of the vacuum line, oxygenfree, purified nitrogen, at a pressure slightly greater than one atmosphere, was introduced into the vessel. Then, the vessel stopcock was removed. Nitrogen gas flowed through the vessel



while plastic tubes were first inserted; then DPPD-LDPE films were introduced into the vessel. The plastic tubes were designed to prevent transfer of stopcock grease into the vessel, and to guide the films into the empty vessel chamber (C in fig. 1). After film introduction, the stopcock was quickly replaced, and the 1-propanol allowed to thaw. The nitrogen-filled vessel was removed from the vacuum line with the stopcock closed, and the system equilibrated to 22 °C.

At the beginning of an extraction experiment, 1-propanol was introduced into the chamber containing the films by tipping the vessel. The fluorescence intensity of the solution in cell B was observed to increase with time. The intensity was measured at suitable time intervals until no further increase was noted, usually after a week. Between measurements, the vessel was placed in a constant temperature bath at 22 °C, and the alcohol solution was stirred with a magnetic stirrer. To guard against stopcock oxygen leakage, nitrogen was passed through needles piercing a serum cap covering the open arm (A in fig. 1) above the stopcock.

After completion of the 22 °C experiments, control experiments were performed, which established that no additional DPPD was extracted when the system temperature was increased to 60 °C.

### Results and Conclusion

To evaluate the diffusion coefficient  $D$  from measurements of the increasing fluorescence of the 1-propanol solution, fluorescence intensity was plotted as a function of square root of extraction time. For these plots, there was an initial linear increase in fluorescence intensity followed by approach to a horizontal asymptote. From these plots, we obtained the initial slope, and the asymptotic fluorescence intensity,  $F_{\infty}$ . Use of the relation [3]

$$M_t/M_{\infty} = 4/\pi^{1/2} (Dt/\ell^2)^{1/2}$$

(for which  $\ell$  is the thickness of polymer film undergoing extraction,  $t$  is the time in seconds, and  $M_t$  and  $M_{\infty}$  are the amounts of diffusing substance present in the extracting solvent at times  $t$  and at equilibrium respectively) allowed calculation of  $D$  if the ratio  $M_t/M_{\infty}$  was replaced by the ratio of sample fluorescence intensity at time  $t$ ,  $F_t$ , to sample fluorescence intensity after extraction was complete,  $F_{\infty}$ . We verified that in the concentration range of these experiments, fluorescence intensity is linearly related to concentration.

Five independent measurements give a value for  $D$  of  $8.5 \times 10^{-10} \text{ cm}^2/\text{s}$  with a standard deviation of  $0.6 \times 10^{-10} \text{ cm}^2/\text{s}$  for migration of DPPD through LDPE when extracted with a 1-propanol at 22 °C.

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Diffusion of Small Molecules in Polymers  
Subtask 8 of Task 12138

S. S. Chang, J. R. Maurey, and W. J. Pummer

In FY82, besides finishing up the experiments with the migration of  $n\text{-C}_{18}\text{H}_{38}$ ,  $n\text{-C}_{32}\text{H}_{66}$  and 3,5-di-*t*-butyl-4-hydroxytoluene (BHT) from linear and branched polyethylenes, isotactic polypropylene, and (ethylene-vinyl acetate) copolymer into various solvents (NBSIR 82-2472), the following areas of research were undertaken.

Migration of BHT from Impact Modified Polystyrene (IMPS). The rubbery IMPS swells and loses dimensional rigidity by the action of many commonly used fat or oil simulants. Therefore, in choosing a simulant, one should consider the degree of swelling or the retention of the dimensional rigidity. The study also indicated the somewhat limited utility of IMPS in contact with certain types of food.

Migration of Styrene Monomer from Polystyrene. The migration of carbon-14 labeled styrene monomer from so-called "crystal styrene" occurs in the glassy state below the  $T_g$ . The kinetics of diffusion in the glassy state sometimes follows the Case II behavior, such that the initial amount migrated is linearly proportional to time,  $t$ , rather than to  $t^{1/2}$  as in the normal Fickian behavior. The diffusion coefficient in the glassy state is generally several orders of magnitude less than that in the rubbery state.

Absorption of small molecules from Migrant Solutions by Polymers. The migration of small molecules across the polymer/solvent interface may also be studied by the absorption of the migrant by a polymer from the migrant solution. If the absorption is to be monitored by the decrease of the migrant concentration in the solution, then the range of the partition coefficient and the solubility are required to be within certain narrow limits, in order to generate changes that are large enough for a meaningful kinetic study. We have already performed such a study in the case of absorption of  $n\text{-C}_{18}\text{H}_{38}$  by polyethylenes from a 50 percent ethanol solution. Currently the absorption of  $n\text{-C}_{32}\text{H}_{66}$  by polyethylenes from an ethanol solution is under study.

Solubilities of n-Alkanes in Polyolefins and in Various Solvents  
Subtask 9 of Task 12138

S. S. Chang and J. R. Maurey

Solubilities of digomers of linear polyethylene, such as  $n\text{-C}_{18}\text{H}_{38}$  and  $n\text{-C}_{32}\text{H}_{66}$ , in various solvents, as well as in polyolefins, have been determined. The ratios of solubilities in the solvent versus that in the polymer agree well with the partition coefficients as observed by both extraction and absorption experiments reaching equilibrium distribution.

The solubilities of *n*-paraffins in *n*-heptane behave rather ideally. In the ideal case, the solubility as a function of temperature may be predicted from the heat of fusion and the melting points of the solute.



Long chain n-paraffins exist in a rotator phase just a few degrees below the melting point. Solubility measurements on the low temperature phase lead to a hypothetical melting point slightly above the rotator phase transition temperature.

#### Measurements of Relative Diffusion Constants in Polymers Subtask 10 of Task 12138

G. A. Senich

Relative diffusion constants for oligomers, stabilizers, and other low molecular weight compounds in polymers have been obtained by inverse phase gas chromatography (IGC) experiments. This method of polymer analysis provides a convenient way of studying the physical chemistry of interactions occurring between polymers and volatile organic materials or probes. The methodology is very similar to conventional gas chromatography, the principle difference being that a polymer of interest replaces the typical stationary phases used to sorb the vapor-phase probes. The experiment involves injecting the probe and an inert marker into a flowing carrier gas stream which propels the substances through a column containing the polymer, coated on an inert support packed within the column. The time lag between injection and elution of the vapor peak and its width or standard deviation characterize the polymer-probe interactions, which are strongly influenced by the carrier gas flow velocity. The steady-state probe distribution reached between vapor and polymer phases at low flow rates allows polymer-probe thermodynamics to be studied. A steady-state distribution is not reached at high flow rates where the kinetics of polymer-probe interactions are accessible and the probe diffusivity in the polymer can be obtained as described below.

Chromatographic peak broadening is commonly quantified by the height equivalent to a theoretical plate, which can be calculated from the standard deviation and, ideally, is proportional to the carrier gas flow velocity at high velocities. This constant of proportionality,  $C$ , is related to the diffusivity of the probe in the polymer,  $D$ , by the following expression:

$$D = 2d^2k/[3C(1 + k)^2] = Yk/[C(1 + k)^2]$$

where  $d$  is the thickness of the polymer layer and  $k$  is the column capacity factor derived from the time lag. If  $C$  and  $k$  are determined by IGC experiments and  $d$  is known from the geometry of the polymer in the column, the polymer-probe diffusion coefficient can be obtained from the equation. Several problems have been identified in determining the diffusivity in this manner. The equation applies only to peak spreading in localized areas of the column, although the average velocity is often used in its application. Gas phase diffusion can also contribute to peak spreading and, in turn, to the  $C$  value found at high carrier flow rates. In addition, any calculation of  $D$  is very sensitive to the distance over which diffusion occurs,  $d$ . The value of  $d$  used in the equation can vary widely, depending on whether the polymer is distributed as a thin, uniform film or in much thicker regions, although previous studies [1,2] have indicated that the latter geometry is favored. These complications make absolute diffusivities difficult to determine by IGC, however, if several probes are studied in the same column,



the diffusivity of one probe in the polymer can be compared to that of another irrespective of the method of calculating the absolute diffusivity. Such IGC experiments have been conducted; the C and k values for selected alkane probes are given in the table below. This information can be used to obtain relative diffusivities by splitting the equation into two terms: the first describing the polymer geometry only and the second characterizing the polymer-probe interactions. The first term is constant in all determinations with a particular column and is abbreviated as Y. This form of the equation was used to determine the probe diffusivity values given in column four of the table. By selecting one of the probes as a reference, in this case octadecane, the diffusivity of a probe in the polymer relative to the diffusivity of the reference can be obtained from a ratio of the respective results, also given in the table. An absolute diffusion constant for each probe in the polymer can be obtained from the relative diffusivity values if an absolute diffusion coefficient for any of the probes in that polymer exists. Using the previous value of  $2.4 \times 10^{-7}$  cm<sup>2</sup>/s for octadecane in HPDE [2], the absolute diffusivities indicated can be obtained by multiplying the relative diffusion coefficients by this factor.

#### Relative Diffusivity of Alkanes in HDPE at 150 °C

Probe <sup>a</sup>	C(ms)	k	D <sub>Probe</sub>	D <sub>Probe</sub> /D <sub>C<sub>18</sub></sub>	D(10 <sup>7</sup> cm <sup>2</sup> /s)
C <sub>18</sub>	21.9	119.	0.38 Y	1.	2.4
C <sub>16</sub>	7.8	60.9	2.05 Y	5.4	13.
MeC <sub>15</sub>	8.7	49.0	2.25 Y	6.0	14.
Me <sub>7</sub> C <sub>9</sub>	18.	12.8	3.74 Y	9.9	24.
C <sub>13</sub>	12.	12.1	5.74 Y	15.2	36.

<sup>a</sup>C<sub>18</sub> = octadecane; C<sub>16</sub> = hexadecane; MeC<sub>15</sub> = 2-methylpentadecane; Me<sub>7</sub>C<sub>9</sub> = 2,2,4,4,6,8,8-heptamethylnonane; C<sub>13</sub> = tridecane.

Relative and absolute diffusion coefficients can be utilized in a large number of industrial applications, such as in modeling the controlled release of bioactive substances, estimating the amounts of oligomers, plasticizers, and antioxidants migrating or leached from polymers over time, and designing membrane separation processes.

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#### Measurement of Antioxidant Diffusion by Microfluorimetry Subtask 11 of Task 12138

F. W. Wang and B. F. Howell

The diffusion of the antioxidant N,N'-β-dinaphthyl-p-phenylene-diamine (DNPD) in branched polyethylene (PE) SRM 1476 is being measured by microfluorimetry according to the procedure briefly described as follows.

Two thin rectangloids of PE, one of which contains 0.002 percent w/w of DNPd, are placed side by side in a close fitting Teflon frame, with the thin sides adjacent and in contact. The combination is sandwiched between two pieces of microscope cover glass, compressed with a spring, and heated in an evacuated chamber. After melting, followed by quenching, the DNPd concentration approximates a step function which broadens in time with diffusion at a specified temperature. Concentration profiles are measured with a microfluorimeter to yield the diffusion coefficient  $D$  of DNPd in PE.

Experiments at 70 °C led to a reasonable value of  $D$  for DNPd in PE. However, because of the limited solubility of DNPd in PE, aggregation of DNPd often took place in places corresponding to the plateau region of the concentration profile. To overcome this difficulty, we have (1) reduced the concentration of DNPd, (2) made certain that the DNPd-containing PE film has uniform antioxidant distribution, and (3) modified the film fusion procedure so as to produce a film of uniform thickness. We anticipate that more accurate values of  $D$  can be obtained because of these procedural improvements. If this is not the case, we plan to use a polymer in which DNPd is more soluble than it is in PE.

Measurement of Translational Diffusion of Polymers by Fluorescence  
Photobleaching Recovery Technique  
Subtask 12 of Task 12138

F. W. Wang and W. H. Grant

The diffusion coefficient of chain molecules is a dynamical parameter which should provide a test of both scaling [1] and reptation [2] concepts proposed by de Gennes. Recently Hervet and co-workers [3] used the forced Rayleigh scattering technique to measure the diffusion coefficient ( $D$ ) of polystyrene chains in benzene. They found that in the semidilute regime where the chains overlap,  $D$  decreases with polymer concentration,  $c$ , as  $c^{-1.7 \pm 0.1}$ , in agreement with scaling law predictions. However, they pointed out that more experiments are necessary to check the molecular weight dependence of the diffusion coefficient.

In collaboration with Professor En-Shinn Wu of the University of Maryland (Baltimore County), we have initiated a project to measure by the fluorescence photobleaching recovery (FPR) technique the diffusion of chain molecules in the semidilute regime. In the FPR technique, one uses high intensity illumination to deplete by photobleaching the observed volume element of chromophore-labeled chain molecules. After the bleaching pulse, the diffusion of unbleached chromophore-labeled chain molecules into the bleached volume element is observed with low intensity illumination. From the time constant for the recovery of the original fluorescence intensity, the diffusion coefficient can be obtained. The FPR technique can be used to measure diffusion coefficients in the range  $10^{-11}$  to  $10^{-6}$  cm<sup>2</sup>/s [4].

We have synthesized a chromophore-labeled polystyrene of narrow molecular weight distribution and measured the diffusion coefficients of this polymer in solutions of unlabeled polystyrene polymers. These experiments showed that the labeled polymer has the appropriate type and extent of labeling



for the FPR technique. However, we were unable to obtain accurate diffusion coefficients because the geometry of the bleached volume element was not adequately controlled. To overcome this difficulty, we have designed and tested a three-compartment cell which has an identical light path for all the compartments. With this cell, the diffusion coefficients of the samples in two compartments can be precisely measured relative to the diffusion coefficient of a standard sample in the third compartment. The absolute diffusion coefficients can then be determined once the absolute diffusion coefficient of the standard sample is determined by an independent method. This novel cell will be used to measure the diffusion coefficients of this and other similarly prepared polymers to check the molecular weight dependence of the diffusion coefficient in the semidilute regime.

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Partition Coefficient of Vinyl Chloride in Poly(vinyl Chloride)  
Subtask 13 of Task 12138

S. S. Chang and W. J. Pummer

Poly(vinyl chloride) (PVC) is one of the most widely used polymers. Its monomer, vinyl chloride also known as VCM, is a recognized carcinogen. The allowable level of VCM in the working atmosphere is regulated by OSHA and EPA. A small amount of VCM is retained by the PVC resin during the polymerization process. By steam stripping, the amount of the residual VCM in the resin may be reduced to less than 1 ppm.

Partitioning as the solubility of VCM in PVC has been studied by several authors at VCM concentrations generally exceeding 10 ppm. As the residual VCM contents in PVC, especially those being used in contact with food, may be made much less than 1 ppm. The study of the Henry's law constant should be extended to the lowest concentrations detectable.

Head-space gas chromatography provides sensitive detection of VCM without serious interferences. The detection limit is about 50 pg with flame-ionization detector. With electron-capture detector and nitrous oxide enhancement, the detection limit may be further lowered.

We have used both manual and automatic injections for the study of the partition coefficient of VCM in PVC down to a concentration about 20 ppb. As the lowest concentration, the partition coefficient observed is still within the order of magnitude as that observed previously for high concentrations.



Further refinements are required to determine more precisely the partition coefficients at low concentrations by reducing the effects of absorption of VCM by Teflon syringe inserts and teflon septum liner, and by estimating more quantitatively the amount sampled in automatic injection operation.

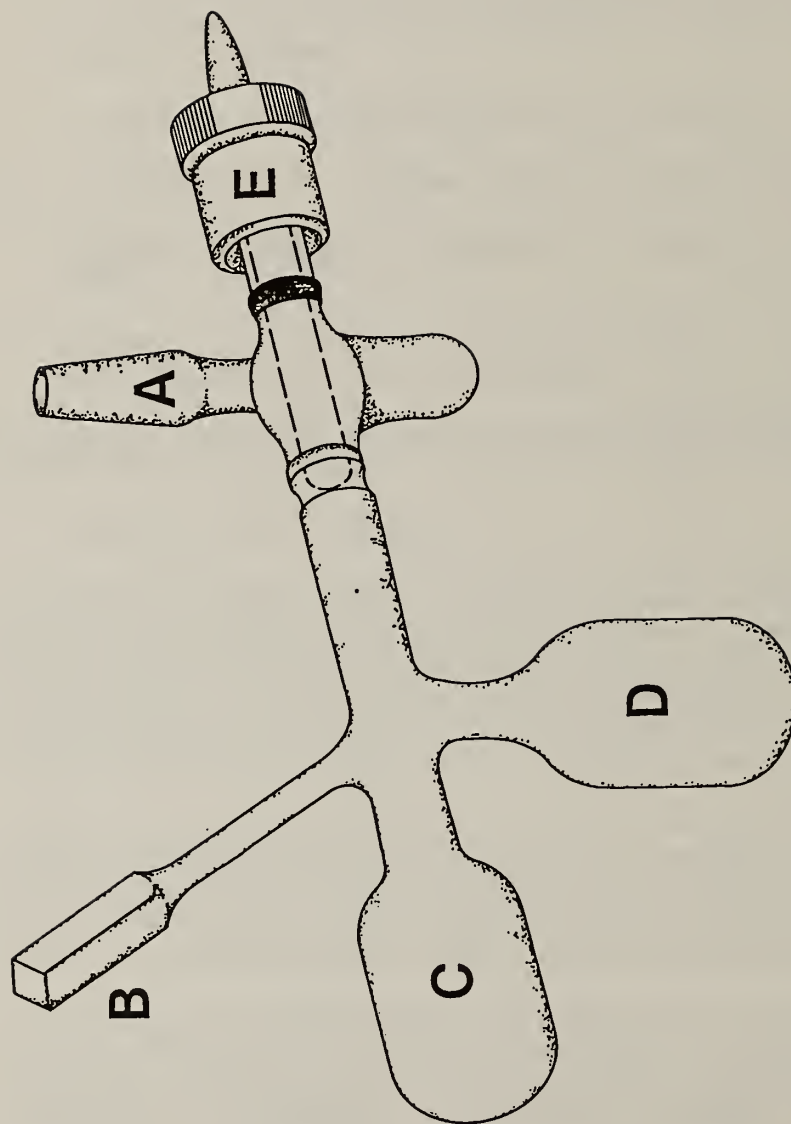


Figure 1 Extraction vessel: A, ground glass joint for connection to vacuum line; B, fluorescence cuvet; C, chamber into which films are introduced prior to extraction; C, chamber into which films are introduced prior to extraction; D, chamber in which solvent is degassed; E, outer part of removable stopcock.

## MICROSTRUCTURE AND PERFORMANCE OF DIELECTRIC PLASTICS

### Task 12139

NBS research in the electrical properties of polymers encompasses a broad range of generic applications from insulating materials with low loss to electronically conducting polymers. Trends in dielectric applications of polymers include higher working voltages in transmission lines to conserve energy and materials, save space, and reduce weight. Among the potential applications for the recently discovered conducting polymers are light weight solid state batteries, electrochemical sensors, and energy conversion. Also included in electrical properties are the piezoelectric and pyroelectric response of polymers which have led to new types of transducers and new measurements. The goal of the task on electrical properties is to carry out long range research to provide the basis for new or improved measurements and provide concepts and data regarding the performance of polymers in high payoff electrical applications. Data, recommendations, and basic scientific concepts resulting from this work go directly to funding organizations through written reports, to manufacturers and users through research associates who work with us, personal communication, laboratory visits, and publication in archival journals.

The study of electrical conduction of organic polymers is a major new frontier in solid state physics. Most current research involves an empirical search for improved dopant-polymer combinations from a bewildering array of compounds. Chemical structure-electrical property correlations are not yet evident. The key need is for a better knowledge of the molecular packing, dopant locations, chemical changes with doping, molecular orientation, and charge carrier pathways to form a basis for modeling and predicting electrical properties. This work is ideally suited to NBS because it involves long range research on improved measurements, standards, test methods, and scientific concepts. Good progress has been made in an appreciable initial effort on electronic conduction.

Applications of polarized polymers as pyro- and piezoelectric transducers are rapidly growing. Transducer manufacturers as well as private and Government transducer users (DOD, EPA, HHS) need reliable basic information connecting polymer structure and polymer performance to the design of improved transducers. This work provides the scientific basis for transducer material and device manufacturers to design and develop commercial polymer transducers for use in a wide range of generic applications.

Important scientific opportunities of this work include breakthroughs in understanding the basic factors in electrical failure of polymers and discovery of novel measurement techniques which are becoming possible with newly developed polymers. For example, on-going work will show how polymers interact with electronic and ionic charges and how structure modification alters piezoelectric and semiconducting properties.



Fast ion transport in polymers provides a basis for a large and growing class of important applications including production of chlorine and caustic from brine, hydrogen production from low-head hydroelectric or ocean thermal energy sources, solid electrolytes for fuel cells and batteries, gas sensors, materials separation membranes, and electrochemical devices. NBS work is aimed at characterizing the polymer structures, measuring their properties, and relating the structures and properties to provide a scientific basis for predicting specifically and transport mechanisms at the molecular level.

The execution of the task was assisted by Dr. C. Hansen, an industrial research associate from G.E., Dr. G. Harris, a guest worker from the FDA, and by a joint project with Bell Laboratories.

#### Automated Dielectric Measurement

##### Subtask 1 of Task 12139

#### F. I. Mopsik

This activity was begun to develop an efficient, rapid measurement system to characterize dielectric materials. It will allow material studies that were not previously feasible due either to the excessive time and equipment required or the lack of accuracy available.

The instrument being developed will record the transient electric charge response of a dielectric sample to a step change in the applied voltage in real time. This response will be transformed into the dielectric constant and loss over the frequency range of 1 mHz to 10 kHz and plotted by computer.

During FY82 the first version of the system has become operational and its limits examined. As the electronic circuits were completed last year, the only work done was the improvement of the generator to remove its lack of reproducibility at very short times. Improved amplifiers have improved the setting time behavior by a factor of four.

The major work this year has been to develop the transform techniques and the operating programs needed to have a fully operational system. A numerical procedure has been founded and developed that has a basic accuracy of better than 0.1 percent of full scale and can be carried out over 8 decades in frequency in only 1.5 minutes. In addition, a complete set of operating programs has been completed so that measurements to  $10^{-4}$  Hz can now be carried out in less than two hours. A series of measurements as a function of temperature can be completed in less than a week.

Initial measurements have shown that the instrument is capable of detecting a loss peak with a  $\tan \delta$  as low as  $10^{-4}$  from a standard capacitor as well as the loss peak in polypropylene at 10 Hz.

An invited talk at the Gordon Conference on Dielectrics on August 3, 1982 is being presented on the measurement scheme as the latest in the state-of-the-art.

## Dielectric Loss Spectra of Polymers in the Microwave Region

### Subtask 2 of Task 12139

A. J. Bur

This work was undertaken as a result of a direct request from the U.S. Army Civil Engineering Research Laboratory. It consists of a review of dielectric loss data for polymers at microwave frequencies and an illumination of the molecular mechanisms which are responsible for microwave absorption.

A review of the literature reveals that most of the dielectric data for polymers in the frequency range 100 MHz to 100 GHz has been published in the past 15 years. The impetus for this work comes from the communications industry which seeks low loss materials. Well-known low loss dielectrics such as polyethylene, polypropylene, polytetrafluoroethylene, and polystyrene have been measured by several laboratories. Data for other polymers are more difficult to obtain and in some cases do not exist. One of the largest sources of data has been reports from the Massachusetts Institute of Technology, Laboratory for Insulation Research.

The molecular mechanisms responsible for microwave losses are dipoles which are part of a short segment of the main polymer chain or a side chain. A dipole in the amorphous phase is more likely to produce microwave absorption than is one in the crystalline phase.

This work is being assembled as a review and a final report to the Army.

## Resistivity Measurements on Ultra-Drawn Poly(vinylidene fluoride) (PVDF) Films

### Subtask 3 of Task 12139

A. J. Bur

This subtask directly supports the optimization of piezoelectric polymers for applications in industry and Government. It concerns the definition of PVDF properties prior to poling which, after poling, will yield highly active transducers with optimum ageing characteristics.

Thick specimens were prepared by molding PVDF pellets in a compression mold under vacuum. Subsequent preparation steps included annealing or no annealing and various amounts of mechanical drawing ranging from 4:1 to 7:1 draw ratio at 140 °C.

For resistivity measurements, the samples were fitted with guarded electrodes in order to eliminate the effect of surface currents. Several step voltages in the range 75 V to 275 V were applied to each sample and the current was detected using an electrometer or operational amplifier. The current at 10 minutes was used to calculate the resistivity.

X-ray measurements were also made on samples having a range of draw ratios. With these observations we were able to calculate the proportionate amount of  $\alpha$  and  $\beta$  phase crystals in the samples.

The results of the resistivity measurements show two effects: first, the resistivity decreases by a factor of two or four as the unoriented samples are oriented to a 4:1 natural draw ratio; second, the resistivity increases monotonically by over a factor of 10 as draw ratio increases from 4:1 to 7:1. The x-ray measurements show that the resistivity increases as the  $\beta$  phase content increases which indicates that the  $\beta$  phase content increases with draw ratio.

The data reflect the polarization response of the sample to a step voltage. The current is interpreted as that due to a dispersion with a long relaxation time whose origin is dipolar orientation and/or ionic conduction in a Maxwell-Wagner process.

Samples with the highest resistivity are those with the highest draw ratio and high  $\beta$  phase content. We suggest conductivity in these samples is minimized because of the presence of the polar  $\beta$  phase crystals which impede the motion of conducting ions in their neighborhood. These samples are being considered as candidates for optimum transducer activity because high poling fields can be used to polarize the samples and because extremely long relaxation times will inhibit any decrease in activity.

#### Conducting Polymers

##### Subtask 4 of Task 12139

H. P. R. Frederikse, C. K. Chiang, and W. R. Hosler

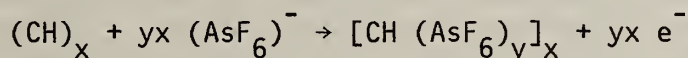
Polymers in which electrical conduction approaches that of metals is a new area of materials science in which there are many unsolved problems but the potential applications are enormous. NBS is making measurements on some of these systems to define the measurement problems for the purpose of improving measurements and developing test methods as well as developing concepts for the conduction mechanism in these materials.

Most of the polymers of interest are not conductive in the as-polymerized state but must be modified. The addition of oxidizing or reducing agents to develop conductivity has been referred to historically as "doping" but this term is probably inappropriate because of the large quantities of added material and the specific oxidation-reduction reactions that occur. At NBS, emphasis has been placed on poly-p-phenylene sulfide, PPS, and polyacetylene,  $(CH)_x$ .

Iodine changes the conductivity of PPS from  $10^{-14}$  to  $\sim 10^{-4}$  S/m at room temperature, but this conductivity decays with time. Apparently, iodine only affects the surface of the PPS film in the early stages of the doping process. For longer periods of time this dopant strongly attacks the polymer and destroys its conductivity as well as its molecular structure.  $AsF_5$  higher and more permanent conductivity in PPS as long as the polymer is kept below 330 K. Measurements between 110 and 330 K yield reproducible values; plots of  $\ln \alpha$  vs  $1/T$  indicate activation energies of 0.09 to 0.14 eV. Optical absorption of pure PPS shows a sharp cutoff at 362 nm or 3.43 eV which probably represents the intrinsic gap between energy bands associated with small  $\pi$ -overlap of the sulfur 3p and carbon 2p electronic states.



Polyacetylene can be made conductive electrochemically which is easily followed by monitoring electrical current and potential. The first phase of this program is to develop the electrochemical doping and modification techniques. This is done via collaboration with E. Blubaugh and W. Yep in Dr. R. Durst's electrochemical group in the Division of Organic Analytical Chemistry. In this year, we have produced polyacetylene electrodes on platinum substrates and in freestanding form. Current-voltage characteristics of these electrodes were measured. For a free-standing  $(CH)_x$  electrode in 0.5 M percent  $LiAsF_6$  propylene carbonate solution, the positive potential at  $(CH)_x$  electrode attracts  $AsF_6^-$  toward the  $(CH)_x$  film and dopes the film. The doping reaction can be written as



The extra charges were removed at the electrode through the external circuit. The doping current increased monotonically as the applied potential increased up to 2.0 volts. On the reducing of applied potential, the electrochemical current showed a peak at 0.4 volt. This suggests that the dopants are electrochemically bound to the polyacetylene. A similar response was seen in the graphite intercalation. By continuing to apply a positive potential, we can dope  $(CH)_x$  to a highly conducting state. The electrochemical response of highly doped polyacetylene is very much like a metal. This electrochemical modification of polyacetylene requires much longer time ( $\sim 10$  h) than that by gas doping (ca. 10 min). Conducting polymers produced in this manner may have very unique physical properties.

Since conductivity is rapidly destroyed by oxygen, the oxidation mechanism of polyacetylene and its kinetic parameters are of interest. Free standing polyacetylene films have been prepared and oxidized in air and in pure oxygen gas at room temperature and at higher temperatures. Infrared spectra of these oxidized samples were measured. An absorption between 3650 and 3200  $cm^{-1}$  was not present in pure polyacetylene and is due to the steady formation of  $-OH$  groups. In most cases of hydrocarbon and polymer oxidation, there is a significant proportion of  $-OOH$  groups (hydro peroxide), which also absorb in this range. The absorption persisted after the sample was heated to 200  $^{\circ}C$  and thus is assigned to hydroxyl groups. Other indicators of the course of the oxidation are the absorptions at 1725 and 1670  $cm^{-1}$ . A general change in the background was observed. Detailed analysis is in progress.

$C^{13}$  NMR spectra were taken of the polyacetylene films oxidized at 50  $^{\circ}C$  for 40 h in air. Heating at high temperature first converted  $(CH)_x$  films from cis-to trans-form. New resonances appear at shifts of  $\sim 58$  ppm,  $\sim 78$  ppm, and 197 ppm. Preliminary assignment of these resonances are: the 58 ppm and 78 ppm resonances are due to  $sp^3$  type carbons and the 197 ppm resonance is due to  $sp^2$  type carbons in carbonyl groups. Detailed consideration of these assignments is also in progress.

The weight increase of polyacetylene due to oxidation was also studied. A sample exposed to air at room temperature for 153 days may increase in weight by over 60 percent. The electrical conductivity decreased to the order of  $1 \times 10^{-12}$  S/m during oxidation.

Structure and Performance of Piezoelectric Polymers  
Subtask 5 of Task 12139

G. T. Davis and M. G. Broadhurst

The objectives of this task are to study the molecular motions, structural changes, and electrical properties associated with the process whereby polymers are made piezoelectric. Information gained from these studies will be used to optimize piezoelectric and pyroelectric response with respect to both initial activity and long-term stability.

While piezoelectric and pyroelectric activity from polymers is comparable to that from good ceramic materials, other properties of polymers often make them the preferred transducer material. Some of the polymer properties which make them so useful include toughness, flexibility, low density, broad band response, close acoustic impedance match to water, and ease of fabrication. Requests for information from other Government agencies and from industries have remained numerous. Interest in this area of research continues at a high level, as evidenced by the 16 papers on this topic presented at the American Physical Society meeting in March 1982, numerous review articles in the literature, and commercial advertisements for polymer transducers in trade journals.

The results of an investigation into the structural changes which occur in a copolymer of vinylidene fluoride and trifluoroethylene (52.8 percent VDF) upon poling and subsequent depoling at elevated temperatures were reported in a series of two publications. The work was a collaborative effort between personnel of the Polymer Science and Standards Division and the Bell Laboratories. An initial mixture of two crystal phases is converted to a single polar phase in which the chain conformation is all-trans. Upon heating to 85 °C, the polymer chains undergo a gradual transition to a somewhat disordered (trans gauche)<sub>3</sub> conformation which has no net polarization. Additional compositions of such copolymers (65/35, 73/27, and 78/22) have been obtained and their properties are now being studied, again in collaboration with Bell Laboratories and Dr. Furukawa at the Institute of Physical and Chemical Research, Saitame, Japan who had been a guest worker at Bell during the previous effort. These copolymers crystallize almost completely in the all-trans conformation but do undergo a phase change to the nonpolar helical conformation at temperatures that get closer to the melting point of the copolymer as the VDF content increases. A study of the properties associated with a ferroelectric Curie point of these polymers may help in understanding why the PVDF homopolymer begins to lose piezoelectric properties at temperatures above 90 °C even though no definite phase changes have been observed prior to the melting of the polymer.

Polarization and Space Charge Studies  
Subtask 6 of Task 12139

A. S. DeReggi, F. I. Mopsik, and A. J. Bur

A measurement method for determining the distribution of space charge or polarization within a dielectric film is now being employed. The method of imparting a thermal pulse to one surface of the sample and following the



transient charge or voltage response as the temperature equilibrates was introduced to NBS by a guest worker (Dr. R. E. Collins from Australia). Recent advances in data acquisition and numerical analysis permits the determination of up to ten Fourier coefficients of the polarization or charge distribution. Details of the analysis have been submitted to the Journal of Applied Physics.

The measurement of polarization and space charge distributions in solid polymers is basic to understanding polymer-charge interactions. In the ferroelectric polymers, these interactions give rise to nonuniform polarization distributions across the thickness of film samples. In the insulating polymers, these interactions are believed to play a key role in the insulating properties, electrical strength and other performance and aging properties. Furthermore, charging phenomena are of basic interest to spacecraft designers concerned with the possibly deleterious effects of space radiation on the spacecraft-borne instruments.

The method has been applied to the study of PVDF when poled at room temperature. The regions of the film near the surfaces were shown to require higher poling fields than the bulk of the film and to remain less poled by approximately 15 percent at fields to 2 MV/cm. When a film was first poled to 2 MV/cm and reverse poled to -1 MV/cm, the center was reverse poled but the surfaces still retained polarization in the original direction with nearly zero mean polarization for the entire sample. A paper on these results has been prepared and has been submitted to the Journal of Applied Physics for publication.

A study has also been done with Professor Sidney Lang of Ben Gurion University. PVDF was poled at low fields at room temperature with Al and Au electrodes to see if work function changes in the electrode materials would influence the poling behavior. Previous work indicated that this could be so. A detailed series of measurements showed that this was not the case but that apparent changes were due to the presence of a small amount of permanent polarization in the original, nominally unpolarized film. The strength of this preexisting polarization varied randomly among samples. Also, the two surfaces of the film were found not to be equivalent. These results reinforce and amplify our previous results that the film is intrinsically nonuniform in its poling behavior. A paper on these results is now in preparation.

Measurements of the polarization distribution in electron-beam charged PVC have proven interesting in that they have suggested a new and potentially useful method of measuring the electric field inside the foil during irradiation. During irradiation, the beam-injected charge is known to give rise to strong electric fields in the polymer. The polymer is believed to become poled under the action of these strong fields, even though the polymer is below its glass transition temperature of approximately 70 °C. Because PVC is a polar material with a linear polarization vs field relation, the distribution of polarization is expected to be proportional to the electric field distribution during irradiation. It turns out that this polarization is stable in time while the injected charge is neutralized or leaves the polymer within a period of a week. We believe that the measurement of the polarization distribution of an electron-beam irradiated PVC sample after it has



discharged for a week under short-circuit conditions yields the electric field distribution which existed during irradiation. Thermal pulse measurements performed so far have shown stable polarization distributions with the qualitative appearance of the calculated electric field distribution during irradiation. Related measurements on PVC samples subjected to known applied voltages have shown that the polymer can be poled below its glass transition, and that the polarizability is of the expected magnitude based on the measured polarization in the irradiated samples and the theoretically predicted field. A manuscript describing this is under preparation.

Spontaneous Polarization in Ferroelectric Polymers  
Subtask 7 of Task 12139

A. S. DeReggi, S. C. Roth, G. T. Davis, and M. G. Broadhurst

A method for measuring the pyroelectric response of polymers as a function of temperature while the temperature is increased linearly with time has been developed at NBS. The technique provides a rapid means of determining the temperature at which polarization begins to decay and is being used to establish the effects of poling variables and polymer morphology on the relative stability of piezoelectric and pyroelectric properties.

Measurements of the sample polarization temperature dependence have been performed on PVDF and on its copolymer with tetrafluoroethylene (TFE). In both cases the polarization has been found to go to zero when melting of the sample is complete, rather than at some transition temperature distinct from the melting temperature. Measurements such as those described here must be done with well characterized samples since the ferroelectric polymers, like other semicrystalline polymers, may exhibit relaxation or melting behavior which depend on the prior mechanical and thermal history. The extended range of temperature over which melting may occur, and the multiphase nature of PVDF samples also must be considered in making the connection between the sample polarization and the spontaneous polarization.

The measurements on biaxially oriented PVDF poled at 100 °C show a gradual loss of sample polarization starting at 70 °C and extending throughout the remainder of the semicrystalline range which finally melts at approximately 170 °C. There is no evidence of ferroelectric to nonferroelectric transition as reported by others, and no sign of impending precipitous polarization decrease of the kind shown by analogous spontaneous magnetization of a ferromagnet near a Curie point. A gradual phase conversion from a polar to an antipolar phase is being considered as an explanation for the gradual loss of sample polarization. The role of defect motion in the conversion and of relaxation of orientation is also being considered as related mechanisms.

Future measurements are planned on the VDF-trifluoroethylene copolymer at high VDF content. A structural-ferroelectric transition distinct from melting is observed in this system at a temperature which depends on composition and possibly on history. Extrapolation of the transition temperature vs composition data to 100 percent VDF would place the transition in PVDF in the area of its melting point. Future measurements

also are planned for poly(vinyl fluoride) which is a semicrystalline system with a single crystalline phase, in which transformation to alternate phases should not exist.

#### Fabrication of Thick Piezoelectric Polymer Film Subtask 8 of Task 12139

A. J. Bur, M. G. Broadhurst, and A. K. Tsao

This subtask results from a direct request from the Navy to explore fabrication of thick piezoelectric polymer film for hydrophone use. Thick film is needed because the voltage response of thin PVDF films is less than typical ceramic hydrophones. The voltage response is inversely proportional to capacitance and hence directly proportional to the thickness of the film. To make the voltage sensitivity of polymers better than that of ceramics the thickness should be at least 750  $\mu\text{m}$ . To process and polarize a film this thick requires special equipment and so far only a couple of European companies have been successful at producing it. In this work, NBS is developing techniques whereby industrial laboratories in the U.S. can process suitable films.

Ultra-drawn PVDF is material which has been stretched beyond its natural draw ratio of 4:1. Using a PVDF sample which has been previously stretched to its natural draw ratio of 4:1, it is possible to obtain draw ratios of 6.5 or 7.0 to 1.0 by reclamping the sample in the Instron machine and stretching at 140  $^{\circ}\text{C}$  at a rate of 0.05 in./min. During the ultra-stretch, the load increases while the sample dimensions decrease, indicating that the modulus increases with increasing draw ratio. The ultra-drawn material is desired because it contains  $\beta$  phase material which poles at lower fields and has a larger polarization than other phases, it is highly oriented, and it is able to withstand high poling fields.

Poling these thick samples requires high voltages. For example, to pole a 0.3 mm thick sample at 2.0 MV/cm, 60 kV are needed. Working at these voltages, it is necessary to suppress corona and flashover conduction by carrying out the poling in oil and to construct the sample electrodes so that high electric fields are not present at the edges.

Ten out of fourteen samples with thicknesses ranging from 0.21 mm to 0.53 mm were successfully poled. These samples had pyroelectric coefficients ranging from 2.1 to 4.1 nC/cm<sup>2</sup>K and hydrostatic piezoelectric coefficients ranging from 8.6 to 15.6 pC/N.

#### Acoustic Sensors Subtask 9 of Task 12139

A. S. DeReggi and S. C. Roth

Measurements employing piezoelectric PVDF transducers in hydrophones and biomedical sensors have shown the polymeric transducers have superior performance characteristics over previously available piezoelectric ceramic devices in terms of a wide operating bandwidth and negligible insertion effects. These favorable characteristics stem from the similarity in acoustic impedance between the PVDF and the common transmission



and test media used in ultrasonics, such as water, oils and, in the case of biomedical ultrasonics, body tissue. There is currently a growing interest in polymer transducers in the ultrasonic community in general and in the biomedical community in particular. The collaboration between NBS and a guest worker from the Bureau of Radiological Health (BRH) has continued during the past year. The principal aims of the collaborative work are the development of polymeric acoustical probes for measuring the radiation pattern of biomedical transducers and the development of improved methods of characterizing the performance of existing biomedical transducers using the new polymeric probes. The knowledge obtainable with the new polymeric sensors can be used to ensure both the safety and adequacy of ultrasonic dosage as well as to advance research in ultrasonic treatment.

A variety of ultrasonic probing hydrophones and hydrophone arrays have been constructed, all featuring the spotpoled, tensioned membrane design configuration which was introduced at NBS several years ago. A patent application which was filed by BRH (November 1980), is still pending, and NTIS has publicized this patent application among ultrasonic manufacturers who might be interested in its commercialization.

In collaboration with NBS, members of the CNR Institute of Clinical Physiology at the University of Pisa are evaluating piezoelectric sensors for the monitoring of cardiac patients. Preliminary clinical data on peripheral pulse signals obtained at Pisa with NBS sensors have been presented at the Computers in Cardiology Conference in Florence in September 1981. These data appear to give useful information about cardiac function, and although this information is complementary to, it is not necessarily contained in EKGs.

#### Fast Ion Transport in Solid State Polymers Subtask 10 of Task 12139

C. K. Chiang, G. T. Davis, A. J. Bur, and A. S. DeReggi

Fast ion transport in solids involves a highly specific interaction between the ionic species and the matrix resulting in transport which is orders of magnitude greater than simple diffusion. Alkali halide complexes with polyethylene oxide show this unique property for cation movement. With financial support from the Office of Naval Research, personnel experienced in electrical properties have recently begun a long range investigation into the relation between the structure and morphology of such polymers and their ability to transport particular ions. These types of polymers have potential high payoff applications as solid state electrolytes for batteries, highly specific electrochemical sensors, and fuel cell separators.

#### Evaluation of Cellulose Acetate as a Neutron Dosimeter Subtask 11 of Task 12139

M. G. Broadhurst, A. J. Bur, and R. B. Schwartz

This problem resulted from a request from the Department of Energy to evaluate a published report that the electrical resistivity of cellulose



acetate was sensitive to the amount of neutron radiation which it has received. If true, this effect could be very useful as a basis for a personal neutron dosimeter.

Several films of cellulose diacetate and triacetate were irradiated with a fluence of about  $3 \times 10^9$  of  $^{252}\text{Cf}$  fission neutrons per square centimeter. We observed decreases in resistivity of at most 10 percent. This, together with the extreme sensitivity of the method to moisture led to the conclusion, in contradiction to a published report, that the resistivity of cellulose acetate would not make a useful neutron dosimeter. This work has been accepted for publication.

#### Electrical Properties of Window Materials for Space Vehicle Re-entry Subtask 12 of Task 12139

H. P. R. Frederikse, A. L. Dragoo, A. H. Kahn, and W. R. Hosler

Since February 1982, NBS has been helping the Defense Nuclear Agency characterize the electric and dielectric properties of high temperature window materials for microwave radiation. The goal of this undertaking is to determine experimentally the high temperature conductivity of the material and to analyze its high frequency dielectric behavior. A prime candidate for windows is hexagonal Boron Nitride (BN), which is a good insulator. If the material is pure, it is expected that intrinsic excitation of electrons will produce a conductivity that can be detected at temperatures higher than 1000 to 1500 °C. Material considerations and other factors probably will limit the measurement range to a maximum of 2500 to 2800 °C. Because BN begins to decompose appreciably at temperatures above 2000 °C (a saturated nitrogen vapor  $p_g$  of one atmosphere is reached at about 2500 °C) measurements must be performed in nitrogen gas at pressures exceeding  $p_g$ . However, our experiments--as well as those of others on oxides, nitrides, etc.--have shown that the gas has an appreciable electrical conductivity which acts as a shunt on the sample resistance. Two techniques have been planned to solve this problem: (1) a sample geometry with "internal" electrodes such that a direct gas conduction path between the two electrodes is being avoided; (2) a guard ring technique combined with an operational amplifier.

The required temperatures up to 3000 °C will be achieved in an electrically heated furnace provided with stacks of tungsten heat shields. Temperatures are measured by means of a W(+aRe) vs W(+bRe) thermocouple as well as an optical pyrometer.

Initial measurements on a BN-sample (hot pressed TS1251--Union Carbide Company) with "internal" electrodes (see above) produced reliable results between 1200 and 2100 K. A plot of log resistance vs  $1/T$  shows a straight line with a slope corresponding to an intrinsic energy gap of 5.2 eV. Due to the unusual sample geometry it is difficult to translate resistance,  $R$ , into resistivity,  $\rho$ .

A computer program has been designed to analyze the response to microwave radiation of a BN window with a high surface temperature and a steep temperature gradient. The large conductivity of the surface layer gives

rise to strong reflection. The transmitted radiation varies in an oscillating function depending on the total thickness of the window material.

This work is expected to contribute to the solution of the long-standing problem of interrupted microwave transmission during atmospheric reentry of rockets.

Other Activities of the  
Polymer Science and Standards Division

Invited Talks

Standardization of Gas Transmission Measurements  
Edgewood Arsenal, Edgewood, MD  
J. D. Barnes  
January 20, 1982

A Computer-Controlled Gas Transmission Measuring Apparatus  
40th Annual Technical Conference, San Francisco, CA  
J. D. Barnes  
May 10, 1982

Standard Reference Materials for Gas Transmission Measurements  
18th State of the Art Symposium, American Chemical Society, Washington, DC  
J. D. Barnes  
June 14, 1982

Bonding at the Polymer/Tooth Surface  
6th Annual Meeting of the Society for Biomaterials, Orlando, FL  
R. L. Bowen  
April 24, 1982

Bonding to Dentin--At Last a Reality  
American Society for Dental Aesthetics, New York, NY  
R. L. Bowen  
May 5, 1982

Electric-Field Induced Changes in the Phase & Orientation of  
Polyvinylidene Fluoride Crystals, IUPAC Macro '82 Conf., Amherst, MA  
M. G. Broadhurst  
July 16, 1982

Piezo- and Pyroelectricity in Polymers  
The Materials Research Society, Boston, MA  
M. G. Broadhurst  
November 16, 1981

Piezoelectric Polymers as Potential Soil Stress Gages  
Air Force Weapons Laboratory, Albuquerque, NM  
M. G. Broadhurst  
January 6, 1982

Overview of Piezoelectricity, Pyroelectricity & Ferroelectricity in  
Polymers  
Workshop on Polymers as Synthetic Metals, Los Alamos, NM  
M. G. Broadhurst  
April 26, 1982

Gruneisen Equation of State for Polymers  
Symposium at Los Alamos National Laboratory, Los Alamos, NM  
M. G. Broadhurst  
April 29, 1982



Initiator-Accelerator Systems for Dental Applications  
ACS Symposium, Las Vegas, NV  
G. M. Brauer  
April 1, 1982

Crystallography and Thermodynamics of Calcium Phosphates Related to  
Biomaterials, Martin Marietta Laboratories, Baltimore, MD  
W. E. Brown  
January 19, 1982

Thermodynamics of Hydroxyapatite Surfaces, 6th Intl. Summer Conference  
on Chemistry of Solid/Liquid, Interfaces, Dubrovnik, Yugoslavia  
W. E. Brown  
June 25, 1982

Fabrication and Characterization of Ultra-Drawn Thick PVDF Transducers  
IUPAC Macro '82 Conference, Amherst, MA  
A. J. Bur  
July 16, 1982

A Dental and Medical Materials Program at NBS  
Johns Hopkins University, Baltimore, MD  
J. M. Cassel  
April 13, 1982

Calorimetric Studies & Spontaneous Thermal Effects in Poly(chloro-  
trifluoroethylene), 11th North American Thermal Analysis Society  
Conference, New Orleans, LA  
S. S. Chang  
October 21, 1981

Topical Fluoridation & Physico-Chemical Mechanisms of Fluoride  
Cariostasis  
University of Alabama Dental School, Birmingham, AL  
L. C. Chow  
November 19, 1981

Crystal Structure of Polytetrafluoroethylene as a Function of  
Temperature & Pressure, IUPAC Macro '82 Conference, Amherst, MA  
E. S. Clark  
July 13, 1982

Crystal Structure of the Low Temperature Form (Phase II) of  
Polytetrafluoroethylene, American Crystallographic Assn. Spring  
Meeting  
National Bureau of Standards, Washington, DC  
E. S. Clark  
March 29, 1982

A New Test Method for Determining the Environmental Stress-Crack  
Resistance of Ethylene Based Plastics,  
ASTM Subcommittee D20.12.03, Toronto, Canada  
J. M. Crissman  
June 23, 1982

Field Induced Phase Transitions & Piezoelectricity in Vinylidene Fluoride

Polymers and Copolymers, IUPAC Macro '82 Conference, Amherst, MA

G. T. Davis

July 16, 1982

Polarization Distribution in PVF<sub>2</sub> as Measured by the Thermal Pulse Method and Recent Results on the Piezoelectric Retention Characteristics of PVF<sub>2</sub> Upon Heating to Melting

Thomas-CSF, Laboratoire Central de Recherches, Orsay, France

A. S. DeReggi

September 14, 1981

High Temperature Measurements of the Pyroelectric Response of PVF<sub>2</sub> Computers in Cardiology Conference, Florence, Italy

A. S. DeReggi

September 23, 1981

Review of NBS Work on Piezoelectric Polymers & Its Relevance to Ultrasonics

Instituto di Acustica O.M. Corbino, Rome, Italy

A. S. DeReggi

September 28, 1981

Piezoelectric Properties of Synthetic Polymers and Their Applications University of Pisa, Facoltà di Ingegneria, Pisa Italy

A. S. DeReggi

September 30, 1981

Measurement of Charge Distribution in Polymer Films

Gordon Research Conference on Polymers, Ventura, CA

A. S. DeReggi

January 11, 1982

Electric Field Distribution in Electron Beam Irradiated PVC

California Institute of Technology, Pasadena, CA

A. S. DeReggi

January 12, 1982

Ferroelectric Properties of PVF<sub>2</sub> and Copolymers and Their Potential Uses in Ultrasonics and Biomedicine

Johns Hopkins University, Laurel, MD

A. S. DeReggi

February 10, 1982

High Temperature Measurements of the Pyroelectric Response of PVF<sub>2</sub> American Physical Society Meeting, Dallas, TX

A. S. DeReggi

March 8, 1982

Piezoelectric and Pyroelectric Properties of Synthetic Polymers and Their Applications in Transducers

Southwest Research Institute, San Antonio, TX

A. S. DeReggi

March 12, 1982

Real-Time Processing of Data and Subsequent Feedback in Computer-  
Controlled Thermogravimetry  
Eastern Analytical Symposium, New York, NY  
B. Dickens  
November 19, 1981

The U.S. Polymer Industry & the Polymer Science & Standards Division  
The Institute of Chemistry, Beijing, China  
R. K. Eby  
September 30, 1981

Structures and Disorder in the Phases of Polytetrafluoroethylene  
The Institute for Chemistry, Beijing, China  
R. K. Eby  
October 4, 1981

The U.S. Polymer Industry & the Polymer Science & Standards Division  
The Institute for Applied Chemistry, Changchun, China  
R. K. Eby  
October 6, 1981

Structures and Disorder in the Phases of Polytetrafluoroethylene  
The Institute for Applied Chemistry, Changchun, China  
R. K. Eby  
October 7, 1981

Structures and Disorder in the Phases of Polytetrafluoroethylene  
Northwest University, Xian, China  
R. K. Eby  
October 10, 1981

Structures and Disorder in the Phases of Polytetrafluoroethylene  
The Institute for Organic Chemistry, Shanghai, China  
R. K. Eby  
October 11, 1981

The U.S. Polymer Industry & the Polymer Science & Standards Division  
Fu Dan University, Shanghai, China  
R. K. Eby  
October 12, 1981

The Structures and Disorder of the Phases of Polytetrafluoroethylene  
Pittsburgh Diffraction Conf., Cleveland, OH  
R. K. Eby  
November 5, 1981

The U.S. Polymer Industry & the Polymer Science & Standards Division  
Indian Institute of Technology, Delhi, India  
R. K. Eby  
February 2, 1982

Structures and Disorders in the Phases of PTFE  
University of Delhi, Delhi, India  
R. K. Eby  
February 4, 1982



The U.S. Polymer Industry & the Polymer Science & Standards Division  
National Aeronautical Laboratory, Bangalore, India

R. K. Eby  
February 8, 1982

Structures and Disorders in the Phases of PTFE  
National Aeronautical Laboratory, Bangalore, India

R. K. Eby  
February 8, 1982

Characterization of Polymeric Materials with Emphasis on NDE for  
Degradation & Failure  
DARPA Workshop on Nondestructive Evaluation of Polymers & Polymer-  
Based Composites, Wrightsville Beach, NC

R. K. Eby  
April 28, 1982

Disorders in the Crystal Structures of Homo- & Copolymers of  
Polytetrafluoroethylene, IUPAC '82 Macro Conference, Amherst, MA

R. K. Eby  
July 13, 1982

Durability of Polymers  
DARPA Matls. Res. Council Workshop on Polymer Opportunities,  
La Jolla, CA

R. K. Eby  
July 23, 1982

The Polymer Science & Standards Division of NBS  
Martin Marietta Laboratories, Baltimore, MD

R. K. Eby  
September 1982

Overview of the Polymer Science & Standards Division  
3M Company, Minneapolis, MN

R. K. Eby, M. G. Broadhurst, G. T. Davis, F. W. Wang, B. M. Fanconi,  
and I. C. Sanchez  
September 21, 1982

Overview of the Polymer Science & Standards Division  
Xerox Corporation, Toronto, Canada

R. K. Eby, M. G. Broadhurst, G. T. Davis, F. W. Wang, B. M. Fanconi,  
and I. C. Sanchez  
September 23, 1982

Overview of the Polymer Science & Standards Division  
National Research Council, Ottawa, Canada

R. K. Eby, M. G. Broadhurst, G. T. Davis, F. W. Wang, B. M. Fanconi,  
and I. C. Sanchez  
September 24, 1982

Fourier Transform Infrared Spectroscopy of Polymers. Theory & Application  
Symposium on FTIR Techniques in Plastics Characterization & Processing, ASTM, Williamsburg, VA  
B. M. Fanconi  
March 16, 1982

Chain Scission and Mechanical Degradation of Polyethylene  
IUPAC Macro '82 Conference, Amherst, MA  
B. M. Fanconi  
July 14, 1982

Calculations of Defect Structure in Polytetrafluoroethylene  
IUPAC Macro '82 Conference, Amherst, MA  
B. L. Farmer  
July 13, 1982

Role of Thermal Analysis in the Lifetime Prediction of Polymers  
Second European Symposium on Thermal Analysis, Aberdeen, Scotland  
J. H. Flynn  
September 3, 1981

Mettler Award Address  
Royal Society of Chemistry, Salford, England  
J. H. Flynn  
September 7, 1981

Study of Degradation of Polymers by Thermogravimetry  
Chemical Society of Vojvodina, Novi Sad, Yugoslavia  
J. H. Flynn  
September 15, 1981

Comments on Two Enigmas of Condensed Phase Kinetics--The Compensation Effect and Exact Differential Rate Equations  
11th North American Thermal Analysis Society Conference, New Orleans, LA  
J. H. Flynn  
October 21, 1981

Study of the Degradation of Polymers by Thermogravimetry  
Celanese Research Laboratories, Summit, NJ  
J. H. Flynn  
January 29, 1982

Kinetics of Polymer Degradation  
Polytechnic Institute of New York, Brooklyn, NY  
J. H. Flynn  
May 18, 1982

Lifetime Prediction from Polymer Degradation Kinetics  
IUPAC Macro '82 Conference, Amherst, MA  
J. H. Flynn  
July 15, 1982

The Degradation of Polyurethanes by Thermogravimetry  
7th International Conference on Thermal Analysis, Kingston, Ontario,  
Canada

J. H. Flynn  
August 27, 1982

Dynamic Light Scattering from Polymer Solutions  
Chemistry Institute of Chinese Academy of Sciences, Beijing, China

C. C. Han  
October 4, 1981

Temperature and Molecular Weight Dependence of Polymer Dimensions  
Chemistry Institute of Chinese Academy of Sciences, Beijing, China

C. C. Han  
October 5, 1981

Polymer Molecular Weight Characterization  
Beijing National Institute of Metrology, Beijing, China

C. C. Han  
October 7, 1981

Static Light Scattering Theory  
Beijing National Institute of Metrology, Beijing, China

C. C. Han  
October 8, 1981

Polymer Characterization of Static Light Scattering  
Beijing National Institute of Metrology, Beijing, China

C. C. Han  
October 9, 1981

Static Light Scattering Instrumentation-I  
Beijing National Institute of Metrology, Beijing, China

C. C. Han  
October 10, 1981

Static Light Scattering Instrumentation-II  
Beijing National Institute of Metrology, Beijing, China

C. C. Han  
October 12, 1981

Structure Factor & Second Virial Coefficient of Polymer Solution by  
Light Scattering, Beijing Natl. Inst. of Metrology, Beijing, China

C. C. Han  
October 13, 1981

Small Angle Neutron Scattering from Polymers  
Shanghai Provincial Bureau of Metrology & Eastern Regional  
Measurement Center, Shanghai, China

C. C. Han  
October 16, 1981



Temperature and Molecular Weight Dependence of Polymer Dimensions  
Shanghai Provincial Bureau of Metrology and Eastern Regional  
Measurement Center, Shanghai, China

C. C. Han

October 17, 1981

Static and Dynamic Properties of Polymer Solutions  
Hongzhou Provincial Bureau of Metrology and Zhe-Jiang University  
Hongzhou, China

C. C. Han

October 21, 1981

Temperature and Molecular Weight Dependence of Polymer Dimensions  
Guangzhou Provincial Bureau of Metrology and Zhong-Shan University  
Guangzhou, China

C. C. Han

October 23, 1981

Light Scattering & SANS from Polymers and Polymer Solutions  
Guangzhou Provincial Bureau of Metrology and Zhong-Shan University  
Guangzhou, China

C. C. Han

October 24, 1981

Effects of Excluded Volume and Pre-averaging of Oseen-Tensor for Dilute  
Polymer Solutions by Dynamic Light Scattering

Dept. of Macromolecular Science, Osaka University, Japan

C. C. Han

November 4, 1981

Small Angle Neutron Scattering from Polymers

UBE Industry, Osaka, Japan

C. C. Han

November 5, 1981

Dynamic Light Scattering from Dilute Polymer Solutions

Dept. of Polymer Chemistry, Kyoto University, Japan

C. C. Han

November 6, 1981

Dynamic Light Scattering from Dilute Polymer Solutions in the  
Intermediate  $q$ -region

Dept. of Synthetic Chemistry, Nagoya University, Japan

C. C. Han

November 9, 1981

Small Angle Neutron Scattering from Polymers

Institute of Materials Science, University of Connecticut, Storrs, CT

C. C. Han

December 4, 1981

Cooperative and Self-Diffusion of Polymers in Semidilute Solutions  
by Dynamic Light Scattering  
Dept. of Nuclear Engineering, University of Michigan, Madison, WI  
C. C. Han  
April 5, 1982

Dynamic Light Scattering of Polymer Solutions in the Semidilute Region  
Dept. of Chemistry, University of Wisconsin, Madison, WI  
C. C. Han  
April 7, 1982

Small Angle Neutron Scattering from Polymers  
Dept. of Chemistry and Chemical Engineering, Virginia Polytechnic  
Institute and State University, Blacksburg, VA  
C. C. Han  
May 12, 1982

Dynamic Light Scattering from Dilute and Semidilute Polymer Solutions  
Ann Arbor Conference on Quasielastic Light Scattering Spectra & Their  
Interpretations, Ann Arbor, MI  
C. C. Han  
June 23, 1982

Plastisol Characterization  
Office of Naval Research Review on Compliant Coating Drag Reduction,  
Naval Research Laboratory, Washington, DC  
D. L. Hunston  
October 15, 1981

Fundamental Aspects of Adhesion  
Workshop on Engineering with Adhesives, East Brunswick, NJ  
D. L. Hunston  
October 26, 1981

Developing Failure Criteria for the Polymers Used in Structural  
Adhesives and Composites  
SPI Meeting on Reinforced Plastics/Composites, Washington, DC  
D. L. Hunston  
January 15, 1982

Mechanics of Adhesive Bond Failure  
Center for Professional Advancement, San Mateo, CA  
D. L. Hunston  
February 10, 1982

Durability and Adhesive Bond Failure  
Center for Professional Advancement, San Mateo, CA  
D. L. Hunston  
February 10, 1982

Comparison Between Fracture Behavior in Adhesive Bonds & Fibrous  
Composites Adhesion Society Meeting, Mobile, AL  
D. L. Hunston  
February 23, 1982

Mechanical Properties and Failure Behavior of Toughened Glassy Polymers  
Symposium, Civil Engineering Dept., Texas A&M University,  
College Station, TX  
D. L. Hunston  
February 25, 1982

Fracture Behavior of Adhesives and Composite Matrix Resins  
General Dynamics Research Laboratories, Ft. Worth, TX  
D. L. Hunston  
February 26, 1982

Crack Propagation in Rubber-Toughened Epoxy  
International Conf. on Deformation, Yield & Fracture, Cambridge, England  
D. L. Hunston and A. J. Kinloch  
March 31, 1982

General Rheology and Its Applications in Adhesion  
Workshop on Adhesion and Adhesives, Kent State University, Kent, OH  
D. L. Hunston  
June 7, 1982

Flow Fundamentals in Fluid Systems Containing High Molecular Weight  
Additives  
Symposium on Applied Rheology for the Industrial Chemists, Kent  
State Univ., Kent, OH  
D. L. Hunston  
June 24, 1982

Fracture Behavior of Brittle Materials  
Symposium on Applied Rheology for the Industrial Chemist  
Kent State University, Kent, OH  
D. L. Hunston  
June 25, 1982

Cure Monitoring of Thermosetting Polymers by Ultrasonics  
AF-NAVY/DARPA Review on Quantitative NDE, San Diego, CA  
D. L. Hunston  
August 6, 1982

Characterization of Fracture Behavior of Adhesive Joints  
ACS International Symp. on Adhesive Joints, Kansas City, MO  
D. L. Hunston  
September 15, 1982

Mechanics of Fracture for Adhesive Joints  
ACS International Symposium on Adhesive Joints, Kansas City, MO  
D. L. Hunston and S. S. Wang  
September 15, 1982

Rheology of Cure for Intaglio Printing Inks  
ACS Symposium on Chemorheology of Thermosetting Polymers,  
Kansas City, MO  
D. L. Hunston  
September 16, 1982



The Morphology of Polymers  
31st Annual Meeting, Society of Polymer Science of Japan, Tokyo, Japan  
F. A. Khoury  
May 30, 1982

The Morphology of Polyethylene Crystals Grown from Solution at High  
Temperatures, Kyoto University, Kyoto, Japan  
F. A. Khoury  
June 2, 1982

The Crystallization and Morphology of Polymers  
Osaka University, Osaka, Japan  
F. A. Khoury  
June 3, 1982

The Morphology of Polymer Crystals Grown From Solution  
UBE Plastics Laboratory, Hirakata, Japan  
F. A. Khoury  
June 4, 1982

The Morphology of Polymer Crystals Grown from Solution  
Kyushu University, Fukuoka, Japan  
F. A. Khoury  
June 8, 1982

Dynamic Light Scattering in the Intermediate Momentum Transfer Region  
National Institutes of Health, Bethesda, MD  
T. P. Lodge  
November 19, 1981

Conformation and Dynamics of Polymers in Solution  
University of Iowa, Iowa City, IA  
T. P. Lodge  
January 18, 1982

Conformation and Dynamics of Polymers in Solution  
University of Pittsburgh, Pittsburgh, PA  
T. P. Lodge  
January 20, 1982

Conformation and Dynamics of Polymers in Solution  
Carnegie-Melon University, Pittsburgh, PA  
T. P. Lodge  
January 21, 1982

Conformation and Dynamics of Polymers in Solution  
University of Georgia, Athens, GA  
T. P. Lodge  
January 26, 1982

Conformation and Dynamics of Polymers in Solution  
Georgia Institute of Technology, Atlanta, GA  
T. P. Lodge  
January 28, 1982

Conformation and Dynamics of Polymers in Solution  
Purdue University, West Lafayette, IN  
T. P. Lodge  
February 1, 1982

Conformation and Dynamics of Polymers in Solution  
Dartmouth College, Hanover, NH  
T. P. Lodge  
February 8, 1982

Conformation and Dynamics of Polymers in Solution  
University of Illinois, Urbana, IL  
T. P. Lodge  
February 12, 1982

Conformation and Dynamics of Polymers in Solution  
Cornell University, Ithaca, NY  
T. P. Lodge  
February 17, 1982

Conformation and Dynamics of Polymers in Solution  
University of Michigan, Ann Arbor, MI  
T. P. Lodge  
February 19, 1982

Conformation and Dynamics of Polymers in Solution  
University of Minnesota, Minneapolis, MN  
T. P. Lodge  
February 22, 1982

Conformation and Dynamics of Polymers in Solution  
University of California, Berkeley, CA  
T. P. Lodge  
February 24, 1982

Dynamic Light Scattering in the Intermediate Momentum Transfer Region  
APS Meeting, Dallas, TX  
T. P. Lodge  
March 11, 1982

Oscillatory Flow Birefringence Properties of Polymer Solutions at  
High Effective Frequencies  
IUPAC Macro '82 Conference, Amherst, MA  
T. P. Lodge  
July 13, 1982

Non-linear Viscoelastic Behavior of PMMA in Torsion  
Centre de Recherches sur les Macromolécules, Strasbourg, France  
G. B. McKenna  
November 10, 1981

Le Compartement Viscoelastique du PMMA sous Torsion  
L'Ecole d'Applications des Hauts Polymeres  
Universite Louis Pasteur, Strasbourg, France  
G. B. McKenna  
March 10, 1982

On the Small Strain Behavior of Crosslinked Natural Rubber in  
Torsion, Extension and Compression  
Malaysian Rubber Producers Research Assn., Brickendonbury, England  
G. B. McKenna  
April 2, 1982

La Variation due Temps a la Rupture du PMMA et du Polyethylene  
L'Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland  
G. B. McKenna  
April 30, 1982

Deviations from Elasticity Theory of Rubber Behavior at Small Strains  
6th European "Network-Group" Mtg., Strasbourg, France  
G. B. McKenna  
July 1, 1982

Adsorption on Hydroxyapatite  
Chemistry Dept., Lucknow University, Lucknow, India  
D. N. Misra  
November 10, 1981

Precision Time Domain Measurements for Audio Frequencies and Below  
Gordon Research Conference on Dielectrics, Plymouth, NH  
F. I. Mopsik  
August 2, 1982

The Role of Dental Materials in Dental Practice  
Dept. of Materials Science, Univ. of Virginia, Charlottesville, VA  
G. C. Paffenbarger  
December 3, 1981

Transport Properties of Highly Drawn Semicrystalline Polymers  
Fiber Society Symp., Princeton University, Princeton, NJ  
A. Peterlin  
May 5, 1982

Mechanical Properties & Morphology of Drawn Semicrystalline Polymers  
IUPAC '82 Meeting, Amherst, MA  
A. Peterlin  
July 14, 1982

History of Polymer Physics  
Gordon Research Conferences, Andover, NH  
A. Peterlin  
July 20, 1982



Transport Properties as an Extremely Sensitive Indicator of the  
Status of the Amorphous Component in the Elastically and Plastically  
Deformed Semicrystalline Polymer

IUPAC Symposium on Polymers, Athens, Greece

A. Peterlin

August 31, 1982

Nature of Fold Surfaces in Lamellar Crystals

European Conference on Polymer Physics, Barcelona, Spain

A. Peterlin

September 22, 1982

Brownian Motion and Polymer Chain Adsorption

Dartmouth College, Hanover, NH

R. Rubin

October 2, 1981

Some Random Walk Questions: Haven't We Been Here Before?

Statistical Physics Seminar, University of Maryland, College Park, MD

R. Rubin

February 16, 1982

Some Far Out Properties of Adsorbed Polymer Chains

University of California, San Diego, La Jolla, CA

R. Rubin

September 1, 1982

Finishing Amalgams

Prevention of Microleakage & Finishing Composite Restorations,

Naval Dental School, Bethesda, MD

N. W. Rupp

September 2, 1981

Esthetic Restorative Materials: Third Generation

Wright-Patterson Air Force Base, Dayton, OH

N. W. Rupp

October 5, 1981

Selection and Use of Dental Materials

Eglin Air Force Base, FL

N. W. Rupp

November 10, 1981

The Selection and Use of Dental Materials

Fresno Madera Dental Foundation, Fresno, CA

N. W. Rupp

December 11, 1981

Research in the Development of Dental Specifications

Georgetown University Dental School, Washington, DC

N. W. Rupp

January 13, 1982

Proper Manipulation of Dental Materials  
Veterans Administration Hospital, Washington, DC  
N. W. Rupp  
January 14, 1982

Dental Cements and Impression Materials  
Naval Graduate Dental School, Bethesda, MD  
N. W. Rupp  
January 28, 1982

Dental Materials for the Fixed Prosthodontist  
Veterans Administration Hospital, Washington, DC  
N. W. Rupp  
February 8, 1982

Dental Research Activities at the National Bureau of Standards  
Dental Hygienists' Association, Wilmington, DE  
N. W. Rupp  
February 16, 1982

Finishing the Amalgam Restoration  
Academy of Operative Dentistry, Chicago, IL  
N. W. Rupp  
February 18, 1982

Impression and Cementation Materials  
Naval Dental School, Bethesda, MD  
N. W. Rupp  
March 1, 1982

Cementation Materials  
Georgetown University Dental School, Washington, DC  
N. W. Rupp  
March 4, 1982

Selection and Use of Dental Materials  
Lackland Air Force Base, TX  
N. W. Rupp  
March 16, 1982

Materials for the Laboratory Technician  
Veterans Administration Hospital, Washington, DC  
N. W. Rupp  
March 23, 1982

Esthetic Restorative Materials  
Georgetown University Dental School, Washington, DC  
N. W. Rupp  
March 25, 1982

Dental Amalgam  
Georgetown University Dental School, Washington, DC  
N. W. Rupp  
April 1, 1982

The Selection and Use of Restorative Dental Materials: Direct and Indirect Techniques  
Research Study Club of Nebraska, Lincoln, NE  
N. W. Rupp  
May 21, 1982

Clinical Significance of Pulp Studies and the Biological Responses to Dental Restorative Procedures and Materials  
West Central District Dental Society's 70th Annual Meeting, Brainerd, MN  
N. W. Rupp  
June 12, 1982

Theory of Phase Equilibria in Polymer Blends  
Rutgers University, Piscataway, NJ  
I. C. Sanchez  
October 9, 1981

Theory of Interfacial Tension in Polymer Mixtures  
Princeton University, Princeton, NJ  
I. C. Sanchez  
December 3, 1981

Theory of Interfacial Tension in Polymer Mixtures  
Kodak Research Laboratories, Rochester, NY  
I. C. Sanchez  
December 9, 1982

Theory of Polymer Blend Phase Behavior  
4th Annual Polymer Summer School, Yugoslav Academy of Sciences, Dubrovnik, Yugoslavia  
I. C. Sanchez  
April 26, 1982

Thermodynamic Properties of Polymer Blends  
Polymer Gordon Research Conference, Colby-Sawyer College, New London, NH  
I. C. Sanchez  
July 5, 1982

Thermodynamic Properties of Polymer Blends  
IUPAC Macro '82 Conference, Amherst, MA  
I. C. Sanchez  
July 12, 1982

Theory of Polymer Interfacial Tension  
Gordon Research Conference on the Science of Adhesion, New Hampton, NH  
I. C. Sanchez  
August 23, 1982

Measurement of Polymer-Solvent Diffusivity by Inverse Gas Chromatography  
Princeton University, Princeton, NJ  
G. A. Senich  
April 10, 1982



What Polymer Chemists Do at the National Bureau of Standards  
Howard University, Washington, DC  
G. A. Senich  
October 7, 1981

Government Careers in Polymer Research at the National Bureau of Standards  
George Washington University, Washington, DC  
G. A. Senich  
October 21, 1981

Characterization of Polymers: Mechanical Property and Diffusion Studies  
NASA Langley Research Center, Hampton, VA  
G. A. Senich  
October 26, 1981

Gas Chromatography of Polymers  
Chemical Society of Washington, Rockville, MD  
G. A. Senich  
February 11, 1982

Chromatographic Studies of Diffusion in Polymers  
IUPAC Macro '82 Conference, Amherst, MA  
G. A. Senich  
July 14, 1982

Measurement of Additive Migration from Plastic Food Packaging  
ISO Consumer Policy Council, Paris, France  
L. E. Smith  
April 27, 1981

Models for Migration of Additives from Polyolefins  
ASTM Technical Seminar, Williamsburg, VA  
L. E. Smith  
March 16, 1982

Castability and Fit of Nonprecious Alloys  
Eastern Maryland Dental Society, Ocean City, MD  
J. A. Tesk  
October 2, 1981

Applications of  $^{13}\text{C}$  NMR to the Characterization of Solid Polymers  
Virginia Polytechnic Institute, Blacksburg, VA  
D. L. VanderHart  
October 1, 1981

NMR Studies of Oriented Polymers, LPE and PET  
Institute fur Physikalische Chemie, University of Mainz, Germany  
D. L. VanderHart  
March 22, 1982

$^{13}\text{C}$  NMR Studies in Solid Polymers  
University of East Anglia, Norwich, England  
D. L. VanderHart  
March 24, 1982

NMR Studies of Oriented Polymers, LPE, and PET  
University of Leeds, Leeds, England  
D. L. VanderHart  
March 26, 1982

$^{13}\text{C}$  NMR of Drawn Polymers  
University of Bristol, Bristol, England  
D. L. VanderHart  
March 29, 1982

High Resolution  $^{13}\text{C}$  NMR of Solid Polymers  
Annual Chemical Congress of the Royal Soc. of Chemistry,  
Birmingham, England  
D. L. VanderHart  
April 2, 1982

$^{13}\text{C}$  NMR in Oriented Polymers  
IUPAC Macro '82 Conference, Amherst, MA  
D. L. VanderHart  
July 12, 1982

Inferences About Molecular Motion in Solid Polymers from Proton-  
Decoupled  $^{13}\text{C}$  NMR  
NMR Minisymposium, Monsanto Research Center, St. Louis, MO  
D. L. VanderHart  
July 20, 1982

NMR in Solid Polymers--An Overview  
24th Rocky Mountain Conference, Society for Applied Spectroscopy,  
Denver, CO  
D. L. VanderHart  
August 3, 1982

Measurement of Polymer-Polymer Compatibility by Non-Radiative Energy  
Transfer Technique  
Gordon Research Conference on the Science of Adhesion, New Hampton, NH  
F. W. Wang  
August 25, 1982

Spectroscopic Study of Amorphous Polyethylene  
Johnson & Johnson Co., Milltown, NJ  
S. L. Wunder  
September 15, 1981

Conformational and Morphological Properties of Polymethylenes  
International Mineral and Chemical Co., Terre Haute, IN  
S. L. Wunder  
November 9, 1981

Conformational and Morphological Properties of Polymethylenes  
Hercules, Wilmington, DE  
S. L. Wunder  
November 12, 1981

Conformational and Morphological Properties of Polymethylenes  
Exxon Research and Engineering Co., Lindberg, NJ  
S. L. Wunder  
November 17, 1981

Conformational and Morphological Properties of Polymethylenes  
Aerojet Strategic Prop., Sacramento, CA  
S. L. Wunder  
December 9, 1981

Conformational and Morphological Properties of Polymethylenes  
E. I. duPont Co., Wilmington, DE  
S. L. Wunder  
December 14, 1981

Interatomic Distances in Al5 Compounds: Geller vs Pearson Hypotheses  
Los Alamos National Laboratory, Los Alamos, NM  
R. M. Waterstrat  
October 7, 1981

Wear Mechanisms in Dental Composites  
American Association of Dental Schools, New Orleans, LA  
W. Wu  
March 16, 1982

Non-Linear Mechanical Behavior of Polymer Solutions at Various  
Concentrations  
IUPAC Macro '82 Conference, Amherst, MA  
L. J. Zapas  
July 15, 1982

#### Seminars for Staff and Guests

Recent Advances in Polyacetylene Chemistry  
Professor Hideki Shirakawa  
University of Tsukuba, Tokyo, Japan  
August 24, 1981

Mechanisms of Rubber Adhesion and Friction  
A. D. Robert  
Malaysian Rubber Producers' Research Association  
Hertford, England  
August 27, 1981

Materials Used in the Lithographic Process  
Dr. Larry Thompson  
Bell Laboratories, Murray Hill, NJ  
September 23, 1981



Polymer Impregnation and Microstructure of Hardened Cement  
Pastes of Various Porosities  
Raouf S. Mikhail  
Ain Shams University, Cairo, Egypt  
September 28, 1981

Disorder in Chain Molecules Observed with Vibrational Spectroscopy  
Dr. R. G. Snyder  
University of California, Berkeley, CA  
November 3, 1981

Scattering Studies of Blends  
Professor Richard S. Stein  
University of Massachusetts, Amherst, MA  
November 19, 1981

On the Role of Liquid Elasticity in Polymer Characterization  
and Journal Bearing Lubrication  
A. S. Lodge  
University of Wisconsin, Madison, WI  
November 24, 1981

Clinical-Pathologic Issues in Cardiac Valve Prostheses and Ventric-  
ular Assist Devices  
Dr. Fred J. Schoen  
Peter Brigham and Women's Hospital, Boston, MA  
December 10, 1981

Renormalization Calculation of the Structure Factor for Polymers  
Professor T. Witten  
University of Michigan, Ann Arbor, MI  
December 12, 1981

Mechano-vibrational Spectroscopy of Polymers  
Professor Shaw Ling Hsu  
University of Massachusetts, Amherst, MA  
December 14, 1981

Time Temperature Equivalence: After All These Years Can It Be Wrong?  
Dr. N. G. McCrum  
University of Oxford, Oxford, England  
March 16, 1982

Mechanism of Physical Aging in Crystalline Polymers  
Dr. N. G. McCrum  
University of Oxford, Oxford, England  
March 16, 1982

Effect of Thermal Parameters on Compatibility in Porcelain  
Veneered Split Metal Rings  
Dr. G. E. O. Widera  
University of Illinois, Chicago, IL  
March 18, 1982

Small Angle Neutron Scattering of a Rubber Network  
Dr. Robert Ullman  
Ford Motor Company, Dearborn, MI  
March 29, 1982

Yield and Fracture of Model Polyethylene Systems  
Dr. David C. Bassett  
University of Reading, England  
March 29, 1982

Crystallization of Polyethylene Copolymers  
Dr. David C. Bassett  
University of Reading, England  
March 30, 1982

Contact Electrification of Polymer Dielectrics & Properties  
at High Electric Fields  
Professor G. Fuhrmann  
University of Kaiserslautern, Germany  
April 1, 1982

The True Biodegradation of Implanted Polymers  
Dr. David F. Williams  
University of Liverpool, England  
April 16, 1982

Polymers for Enhanced Oil Recovery  
Dr. L. Guy Donaruma  
Professor of Chemistry  
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Changes in the Elastic Moduli of Rubber Due to Low Temperature  
Crystallization  
Dr. Andrew Stevenson  
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Brickendonbury, Hertford, England  
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Conformational and Long Branch Analysis by GPC & Laser Light  
Scattering  
Dr. Roger S. Porter  
University of Massachusetts, Amherst, MA  
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Polymer Liquid Crystals/Biaxial Orientation and Its Development in  
Polymer Systems  
Professor James L. White  
University of Tennessee, Knoxville, TN  
May 6, 1982

Synthesis and Characterization of Model Macromolecules  
Professor L. J. Fetters  
Institute of Polymer Science  
University of Akron, Akron, OH  
May 10, 1982

The Synthesis of Hydrophilic Polymers with Nucleic Acid Base Side Chains  
Dr. Charles G. Overberger  
University of Michigan, Ann Arbor, MI  
May 14, 1982

Sliding-Wear Behavior of Dental Restoratives  
Dr. William F. Bailey  
University of Connecticut, Storrs, CT  
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Influence of Molecular Weight Distribution and Catalysts on the Crystallization and Orientation of Polyethylene Terephthalate  
Dr. H. G. Zachmann  
Martin-Luther-King Platz 6  
Hamburg, West Germany  
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Miscibility Behavior of Polyester/Halogenated Polymer Blends  
Dr. R. E. Prud'homme  
Universite Laval, Quebec, Canada  
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The Oxidation of Stabilized Polypropylenes  
Dr. Frank Mayo  
Stanford Research Inst., Stanford, CA  
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Infiltration of Monomers into Hard Tissues  
Dr. N. Nakabayashi  
Tokyo Medical and Dental University, Tokyo, Japan  
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Kineto Rheology, Chemical Change and Rheological Response  
Professor Alex Silberberg  
The Weizmann Institute of Science, Rehovot, Israel  
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Fine Structures of Fibers and Films Made from a Liquid Crystal  
Dr. M. Horio  
Hirakata Plastics Lab., Osaka, Japan  
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Forced Rayleigh Light Scattering of Polymers in Semi-Dilute Solution & Melts  
Madam Liliane Leger  
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Photovoltaic Effect in Ferroelectric Polyvinylidene Fluoride Film  
Professor H. Sasabe  
Tokyo University of Agriculture and Tech., Tokyo, Japan  
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Rheo-Optical Properties of Poly-Alpha-Olefins  
H. Kawai  
Kyoto University, Kyoto, Japan  
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Qualitative and Quantitative Information on Linear Polyethylene  
Fractions as a Function of Molecular Weight  
Dr. Ingrid Voigt-Martin  
Mainz University, Inst. fur Physikalische, West Germany  
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Microphase Separated Structure of Block Copolymers and  
Its Related Properties  
Professor Takeji Hashimoto  
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Time-Dependent Nonlinear Rheological Properties of Entangled Polymer  
Melts and Concentrated Solutions  
Professor David Soong  
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Polarization Switching & Molecular Motion in PVDF & Related Copolymers  
Professor A. Odajima  
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Professor K. Sakaoku  
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Professor I. Mita  
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Professor D. D. Deshpande  
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Thermoluminescence from Irradiated Polymers and Fibers  
Dr. T. Sakai  
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<sup>1</sup>H and <sup>13</sup>C NMR Studies of Solid Polymers

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Mechanical Properties & Morphology of Fiber Glass Reinforced  
Polypropylene Composites

Professor A. Misra

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July 23, 1982

Dynamic Behavior of Polyelectrolytes in Solution

Professor Y. Wada

Yamagata University, Yonezawa, Japan

July 26, 1982

Novel Imaging Techniques for Phase Separated Polymers

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August 11, 1982

Piezoelectricity in Vinylidene Cyanide-Vinyl Acetate Copolymers

Professor S. Miyata

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September 8, 1982

Chemical Characterization of Solid Coals via Magic Angle <sup>13</sup>C NMR

Dr. John Havens

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NDE for Polymer Composites

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Polymer Degradation and Stability (Journal)

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#### Sponsored Conferences

Symposium on Random Walks and Their Applications to the Physical and Biological Sciences, June 28-July 1, 1982 at NBS, Gaithersburg, MD

#### External Recognition

Poster Recognition  
Sybron/Kerr "Milestones in Dentistry--1891-1981  
January 1982  
R. L. Bowen

Honorary Membership  
Omicron Kapper Upsilon Honor Dental Society  
May 1982  
R. L. Bowen

1982 Clemson Award for Contributions to the Technical Literature  
April 1982  
R. L. Bowen

Honorary Membership  
Zeta Zeta Chapter for Omicron Kappa Upsilon  
Georgetown University  
May 1981  
J. M. Cassel

Irwin Vigness Memorial Award for 1982 from the Institute for  
Environmental Sciences for a paper on a fiber optics strain gauge  
S. Edelman

North American Thermal Analysis Society  
J. H. Flynn, Fellow  
October 1981

Royal Netherlands Academy of Sciences  
Corresponding Membership  
H. P. R. Frederikse  
August 1982

Plastics Hall of Fame  
Frank W. Reinhart  
June 1982

#### Patents

Tertiary Aromatic Amine Accelerators Derived from Para-amino  
Phenethanol in Vinyl Monomers  
H. Argentar  
August 18, 1981  
U. S. Patent 4,284,551

Method for Preparing Microporous Glassy Filler Grains for Dental  
Resin Composites  
C. P. Mabie and D. L. Menis  
December 22, 1981  
U. S. Patent 4,306,913

Improved Dental Material  
C. P. Mabie and D. L. Menis  
Filed January 22, 1982

Combinations of Sparingly Soluble Calcium Phosphates in Slurries and  
Pastes as Mineralizers and Cements  
W. E. Brown and L. C. Chow  
Filed April 26, 1982

## Industrial Interactions

### Industrial Research Associates

Exxon Chemical/David Lohse/Charles Han, SANS study of polyolefin blends materials measurement and characterization.

General Electric/Carl Hansen/F. I. Mopsik, Measurement technology using state-of-the-art time domain dielectric spectrometer built at NBS. Work agreed to and agreement being processed for start in September 1982.

Martin Marietta Aerospace/B. N. Ranganathan/L. E. Smith, Characterization of organic composite resin state of cure-measurement technology for processing.

Rheology Research/Elliot Kearsley/R. K. Eby, Design and evaluation of measurement methods for polymer solutions-mathematical modeling of polymer solutions.

American Dental Association/24 Research Associates/J. M. Cassel, Group Leader, Dental and Medical Materials Group, Measurement relevant to dental materials, dental enamel chemistry, caries formation, and caries research.

### Other Industrial Guest Workers

Union Carbide/Park Leung/Charles Han, Sans investigation of polymersurfactant interactions.

Howmedica, Inc./John Saneiki/John Tesk, Evaluation of new NBS bonding test.

Dentsply International/Orville Franklin/John Tesk, Evaluation of New NBS bonding test.

Utah Research Institute/K. W. Zilm/David VanderHart, Effects of Processing Conditions on Polyethylene Terephthalate Fibers.

Williams Gold/James Arnold/John Tesk, Evaluation of New NBS Bonding Test.

### Archival Technical Papers Coauthored With Industrial Employees

Crystalline Forms in a Copolymer of Vinylidene Fluoride and Trifluoroethylene (52/48 mol %)/G. T. Davis and M. G. Broadhurst with Andrew J. Lovinger and T. Furukawa, Bell Laboratories.

Structure and Dielectric Investigation on the Nature of the Transition in a Copolymer of Vinylidene Fluoride and Trifluoroethylene (52/48 mol %)/G. T. Davis and M. G. Broadhurst with Andrew J. Lovinger and T. Furukawa, Bell Laboratories.



$^{13}\text{C}$  NMR in Oriented Polymers/D. L. VanderHart with G. G. A. Bohme and V. D. Mochel, Firestone Tire and Rubber Co.

Surface Thermodynamics of Liquid Polymers: Theory/I. C. Sanchez with C. I. Poser, 3M Company.

Development of test Method for Interlaminar Fracture Energy of Composites/D. L. Hunston, Joint Project with Hercules (C. W. Bascom) and NASA will yield publication.

Publications with American Dental Association authors.

#### Formal Visits

Flexible Packaging Association/5/20/82, Polymers used in packaging-permeation, mechanical durability.

Society of Automotive Engineers/10/81, Mechanical Durability of Polymeric Materials and development of improved test for environmental stress cracking.

Johnson and Johnson Dental Products/3/11/82, 3/18/82 and 6/29/82, Feasibility of licensing adhesive process developed at NBS.

Dentsply, Inc./4/13/82, Dental composite research directions.

Coors Biomedical Co/3/24/82, Dental applications for improved porcelains.

Unitech, Corp./3/4/82, Dental ceramic research.

U.S. Army R&D Command/1/20/82, 5/21/82 and 6/11/82, Polymers used in DOD applications, permeation, characterization, degradation.

Oak Ridge National Laboratory/5/20/82, Degradation of polymers, mechanical properties, characterization.

Defense Advanced Research Projects Agency (DARPA), 3/3/82, NDE, mechanical durability, chemical durability, composites, characterization and electrical properties.

Zarn, Inc. 6/3/82, Mechanical durability, chemical durability, composite, characterization and electrical properties.

NC Science and Technology Research Center, 6/3/82, Mechanical durability, chemical durability, composites, characterization and electrical properties.

Xerox/9/23/82, Overviews of programs.

3M Corp/9/82, Overviews of programs.

National Research Council of Canada, 9/82, Overviews of programs.

#### Participation in Measurement Programs

ASJM Round Robin, High Temperature GPC, Herman Wagner.

ANSI Round Robin, Measurement of Acid Content of PET, Daniel Brown.

ASTM Round Robin, Draft Method for Environmental Stress Cracking of Polyolefins, John Crissman.

ASTM Method D1505, Data for Accuracy of Density of Plastics Measured by the Density Gradient Method, Leonard Bolz and John Barnes.

#### Advisory Activities

Workshop on Ultimate Recycling of Plastics sponsored by Plastics Inst. of America, F. Wang, J. Flynn

Workshop on Polymer Opportunities, sponsored by Defense Advanced Research Projects Agency, R. K. Eby, M. G. Broadhurst, B. M. Fanconi.

Workshop on Polymer Evaluation and Testing sponsored by Defense Advanced Research Projects Agency, R. K. Eby, L. E. Smith, B. M. Fanconi.

Workshop on Soil Shock Sensors sponsored by Department of Defense, M. G. Broadhurst.

Workshop on Electro-Active Polymers sponsored by Los Alamos Laboratory, M. G. Broadhurst.





## METALLURGY DIVISION (564)

R. Mehrabian, Chief

D. M. G. Summers, Secretary

The mission of the Metallurgy Division is to provide data, measurement methods, standards and reference materials, scientific database, and information on the fundamental aspects of processing, structure, physical properties, and performance of metals and alloys to industry, Government agencies, and scientific organizations. The activities of the Division are aimed at a spectrum of technologies with wide generic applications.

The program of the Division involves studies of metals and alloys in order to foster their safe, efficient, and economical utilization to meet our long-term national needs within the larger framework of the materials cycle. Competences are developed and maintained in four general areas: chemical metallurgy with special emphasis on phase diagrams and phase stability; process metallurgy including emphasis on the measurement and science base for innovative processing technologies; quantitative microstructural characterization including nondestructive evaluation (NDE); and properties including friction, wear, and the application of metals as synthetic orthopedic implants. The Division also makes a significant contribution as a national resource of metallurgical information through its Diffusion Data Center and Alloy Data Center. It provides consultation and assistance to other Government agencies and standards organizations in the development of necessary test methods and standards. The programs of the Metallurgy Division are designed to help us meet our future national needs for materials, which will depend in large measure on our response to forces which are now well recognized. Some of these are classical laws of supply and demand; others include such national problems as energy, environment, productivity, the need to foster long-term high-potential payoff technologies, and such international problems as materials availability from third world nations.

For example, our Division, in addition to being involved in theoretical and experimental studies of phase stability, has a joint effort with the American Society for Metals (ASM) to provide critically evaluated phase diagrams to the metallurgical community. The ASM is presently getting a \$4 M commitment from the metals producer and user industries for their contribution to this program. Advancement in the understanding of phase diagrams and the development of predictive models for phase stability are essential in the development of new alloys for our future needs. These could include stronger and lighter alloys for the transportation industry to improve energy cost, new alloys specifically designed to exploit the beneficial effects of innovative new processes such as those referred to as rapid solidification processes, and alloys which would permit substitution for scarce or unavailable elemental constituents. The ASM/NBS program has expanded to include 27 outstanding scientists throughout the world who are assigned the evaluation of specific binary alloy systems. The Metallurgy Division is not only responsible for the overall technical guidance of this program, but has also undertaken to:

- evaluate the important iron, aluminum, and titanium binary systems.
- develop a model computer database system for storage and retrieval of the evaluated phase diagram data.
- develop a computer graphic system for binary and higher order phase diagrams.

A major development during the past year was the appropriation of \$3 M, for one year only, by Congress for expansion of our activities and facilities in Metals Processing. The activities included rapid solidification processing, coatings, and the phase diagram program noted above. The two new metals processes, rapid solidification and coatings, were identified and selected based on existing competences and the high leverage that the Metallurgy Division activities will have on earlier private sector adaptation and exploitation of these emerging technologies. This funding has allowed establishment of advanced metals processing facilities that will be used as part of a continuing program to provide measurements, predictive models, and standards needed for these technologies. Cooperation is being established with industry to supply samples, measure critical data, and provide guidelines to industrial designers who are developing new alloys. During the past year, numerous guest workers, industrial scientists, and distinguished visiting faculty members, such as Professor D. Turnbull of Harvard University, have come to NBS to participate in this program, for periods up to six months, and exchange information concerning these technologies.

The detailed, programmatic content of the Division that follows is described in the four general task areas. The four tasks in the Metallurgy Division are specifically related to two programmatic initiatives (the FY80 Durability and FY82 Metals Processing Initiatives), a competence initiative (the FY80 Synchrotron Initiative), and the major agreement on phase diagrams between the ASM and NBS:

Task 12142--STRUCTURE CHARACTERIZATION. Addresses the Synchrotron Competence Initiative, the application of NDE (Acoustic Emission and Ultrasonics) to materials characterization, and the activities on Analytical Electron Microscopy.

Task 12143--METALLURGICAL PROCESSING. Contains all of the Division's competences in metals processing (e.g., rapid solidification, surface modification, coatings, etc.) and was expanded through the FY82 Metals Processing Initiative. The Diffusion in Metals Data Center is located in this task.

Task 12144--MECHANICAL PROPERTIES AND WEAR. This recently expanded task contains all the Wear activities initiated in the FY80 Durability Initiative. It also contains the research activities on the use of metals as synthetic implants.

Task 12145--CHEMICAL METALLURGY. The Alloy Data Center is in this task. The joint ASM/NBS cooperative agreement utilizes the resources of this task to develop and disseminate critically evaluated phase



diagrams, and on-line computer graphics systems coupled to predictive thermodynamic models. The quarterly ASM/NBS Bulletin of Alloy Phase Diagrams is also published under this task.

The technical activities under the various tasks are closely interrelated and address the overall mission of the Division to meet our present and future societal needs for metals. The central purpose of these scientific activities is to probe the relationships among processing conditions, the internal structure of metals, and their properties and performance. The resulting knowledge can be used to efficiently produce, shape, and otherwise process metals to control their properties and achieve the desired reliable and durable performance in the finished product.

Critical data compilations are being developed and delivered to users concerned with alloy properties, diffusion, and phase diagram information. Standard reference materials are being produced for electron microscope calibration, electron microprobe analysis, and electrical conductivity. Contributions are made to NBS programs in nondestructive evaluation, and artificial implants.

#### FY82 Significant Accomplishments

- Task 12142--STRUCTURE CHARACTERIZATION. This Task's accomplishments are in two major areas: (1) The competence program in which the application of synchrotron radiation to materials science is being investigated. The Metallurgy Division is taking a lead in the construction of hard radiation (0.5 Å to 5 Å) branch lines at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory (BNL) for the Center for Materials Science (CMS) and the Naval Research Laboratory (NRL) scientists to perform unique experiments for research problems in materials science. (2) The new initiative for Metals Processing, where this task's efforts lie in the improvement of microstructure characterization facilities.
- The CMS Synchrotron Radiation Beam Lines at the National Synchrotron Light Source (NSLS) in Brookhaven are being assembled. These include two monochromator tanks, two hutches (experimental stations for small angle scattering and real-time topography) and beam transport mechanisms.
  - A quantitative microscopy facility is being established which includes a new Transmission Electron Microscope (TEM), a Quantimet, and a new x-ray analysis capability for one of our Scanning Electron Microscopes (SEMs), as part of the new effort for Metals Processing.
  - A new four megabyte capacity minicomputer has been installed for analysis of varieties of data ranging from acoustic emission (AE) signals to predictive modeling computation of phase diagrams.
  - A new laser interferometer has been built for microstructure characterization by acoustic emission.



- White radiation topography techniques have been developed and applied to the characterization of Czochralski grown Fe-Al crystals, Ni crystals, Al and Sn powders, Al polycrystals, NaCl crystals, electron beam melted Si crystals,  $Al_2O_3$ , 2024 Al, and human teeth.
- A second generation charge-coupled-device image intensifier for real-time topography has been developed.
- The in-house focused Extended X-ray Absorption Fine Structures (EXAFS) and Surface Extended X-Ray Absorption Fine Structures (SEXAFS) have been used to study various amorphous materials such as metallic glasses and ultra-thin passive films on metals and alloys.

#### Task 12143--METALLURGICAL PROCESSING.

- Major new facilities were designed and put in place in the Metals Processing Laboratory. Facilities are now available to study all three major types of rapid solidification: powder production, ribbon production, and surface treatment. New facilities being added include atomization systems for production of iron, aluminum, and superalloy powders; a hot isostatic press for consolidation of these powders; and a laser system for alloy surface treatment. In addition, electron beam and melt spinning systems were modified to provide significantly improved capabilities for measurement and control of solidification conditions.
- These new facilities are now being used by NBS, industry, other Government agencies, and university workers for innovative studies on metallic glass properties, alloy coatings, surface modifications, and alloy powders, especially as influenced by solidification dynamics. Large interactive programs have been initiated with universities, involving 12 visiting faculty members during the past year, more than 20 students, and contracts with 3 universities for work on metals processing measurement and techniques.
- A new system for producing submicron-size rapidly solidified alloy powders by electrohydrodynamic atomization techniques was used to study solidification dynamics in aluminum alloys subjected to large amounts of undercooling.
- Rapid solidification conditions that produce extended solid solubility in Ag-Cu alloys were determined. Experimental tests at solidification velocities of 100 cm/s yielded single phase alloys having compositions well beyond the equilibrium solubility limit.
- Alloy coatings produced by diffusion-induced grain boundary migration were measured quantitatively with electron microprobe area composition scans. Kinetic mechanisms yielding this new effect were analyzed. Appreciable alloying was achieved in the regions through which the grain boundaries migrated even when oxygen was introduced as an impurity into the regions being alloyed.

- Spatial averaging techniques were applied to ultrasonic pulse-echo measurements developed for in situ determination of positions and velocities of solidification interfaces. The signal-to-noise ratio in large grained specimens where grain scattering problems interfere with interpretation was substantially improved.
- A customized system was designed and put into operation for computerization of bibliographic and other information contained in the Diffusion in Metals Data Center. This system allows detailed searching for diffusion data references according to type of diffusion, alloying elements, and alloy composition.

#### Task 12144--MECHANICAL PROPERTIES AND WEAR.

- Implementation has begun of portions of the new Metals Processing Initiative that pertain to mechanical properties and wear. A plasma transfer arc system is on order that will permit the controlled production of alloy coatings that will be studied next year. New mechanical test and wear test equipment has been identified and will be ordered with expected FY83 funds. Plans for research studies of metal coating properties and performance have been developed including fatigue wear, impact wear, coating adhesion bend strength, modulus, and others.
- The first NBS abrasive wear reference material has been produced and is now available for purchase. This material, D-2 tool steel, will be used to certify abrasive wear testing in industry.
- A new standard practice for conducting solid particle impact erosion tests has been developed with leadership from this task and also approved by the American Society for Testing and Materials (ASTM). This is the first U.S. standard for erosion testing.
- One staff member assumed the chairpersonship of ASTM G2 on Erosion and Wear.
- A new theory of sliding wear was developed at NBS during the visit of two guest workers from the University of Virginia. This new theory predicts wear effects associated with specific material properties, such as flow stress and slip system geometries.
- A microhardness symposium was organized and held at NBS involving presentations of nine research papers in this area. A larger standards-related meeting is being planned for next year.
- Recent galling wear studies on a series of copper-based alloys have shown effects attributed to stacking fault energy variations with composition in the alloys.
- A postdoctoral fellow (National Research Council) has initiated a study of wear effects in titanium alloys, emphasizing fundamental aspects and utilizing analytical electron microscope techniques.



- A new standard was developed with NBS leadership concerning testing of pitting and crevice corrosion of metallic implant materials. This laboratory test will permit assessment of corrosion-resistance differences between alloys for implant related applications.
- Experiments and theoretical studies are in progress concerning interface strengths at metallic implant surfaces bonded to polymer materials. Analysis has shown torsional loading effects as being a critical concern in certain implant device applications.
- Laboratory corrosion studies of cobalt-based alloys used in implant applications have shown a strong effect of the concentration of iron (a minor alloying element) on performance.
- Studies of the effect of several surface treatments on the corrosion fatigue life of titanium implant alloys in saline solution have shown a beneficial response of particular mechanical surface roughing treatment, presumably resulting from deformation patterns induced into the surface regions.

#### Task 12145--CHEMICAL METALLURGY.

- Four issues of the Bulletin of Alloy Phase Diagrams are now published each year. Graphics have been prepared at NBS and computer files for the published systems are maintained on the UNIVAC 1100/82. Approximately 80 new binary diagrams have been entered.
- A freely formatted data structure has been developed which can be used for phase diagram, crystal structure, lattice parameter, and thermodynamic data. A preliminary report on the high level computer language (LISP) based structure was made at the Computer Calculation of Phase Diagrams (CALPHAD) conference (May 1982).
- Evaluation of Ti-systems has been continued. All Ti-transition and Ti-noble metal systems will have been completed by September 30, 1982 and the evaluations published together as a report to the Office of Naval Research.
- Two major new systems of Al-binary alloys and Fe-binary alloys have been initiated. The systems Al-Li, Al-Be, Al-Mg, and Al-Zn have been completed. The systems Al-Cd, Al-In, Al-Ga, Al-Cu, and Fe-Ru are in progress.
- Development of predictive modeling has been vigorously pursued. Updated thermodynamic software have been obtained from the Stuttgart group and necessary modifications to the user interface are underway. Dr. Bo Sundman of the Royal Institute of Technology, Stockholm, will visit our data center in November 1982 to provide us with computer programs to use sublattice models.
- The feasibility of predictive modeling of metastable phase regions has been demonstrated. Systems of interest for rapid solidification processing which have been modeled are Ti-Fe, Ti-Co, Ti-Ni, Al-Mg, Al-Li, and Al-Zn.



- Technique to produce very low oxygen (< 250 ppm) content Ti alloys was developed to resolve conflicting reports of several Ti phase diagrams in the literature.
- A Differential Scanning Calorimeter (DSC) was obtained to enhance the experimental capabilities. This apparatus will be used as a tool to accurately determine transformation temperatures and heats of transformation in Ti-Al-Mo phase diagrams.
- Ti-Al edge of the ternary Ti-Al-Mo diagram has been mapped, using TEM, magnetic susceptibility, and DSC techniques.
- Alloy tempers and plate thicknesses that are most likely to contain soft spots due to specific processing errors for 2024 aluminum plates have been delineated.
- A model to predict macrosegregation in ingots of 2024 aluminum alloy was developed and its usefulness to predict macrosegregation in laboratory ingots of 2024 aluminum alloy was demonstrated.
- A set of experimental C-curves was determined from which the alloy properties can be established for any time-temperature cycle during quench from solution annealing treatment.
- Fundamental understanding of the relative solid solubility of two transition metals has been advanced.
- A new understanding of volume effects in transition-metal alloying has been provided.

The results of our metallurgical research are communicated to the scientific community through technical publications, lectures, active participation of Division members on various national and international committees, personal contacts, and the organization and sponsorship of conferences and meetings on various subjects such as acoustic emission, synthetic implants, alloy phase formation, solidification, wear, and mechanical failure prevention. For example, the personnel in the Division serve on numerous ASTM Committees, including Chairperson of the B-6 Committee, Chairperson of Committee G-2, and Past Chairperson of Committee E-42, and chairperson of several subcommittees. The staff participated on a number of National Materials Advisory Board (NMAB) studies including Chairperson of the Rapid Solidification Processing Committee. The technical staff have organized and chaired several international conferences on NDE, Wear and Processing. For example, the Third Conference on Rapid Solidification process to be held at NBS in late 1982 will be chaired by our staff. The Metallurgy Division's staff serve on over 60 other national professional and technical committees.

The Metallurgy Division also acts as coordinator of a variety of industry/academia/Government workshops. It coordinated and co-sponsored with Committee on Materials (COMAT) the 1981 Briefing/Workshop on Rapid Solidification Technology, with the proceedings being published as an NBS report in FY82. In July 1982, a Briefing/Workshop on the development of process control sensors for the steel industry was organized and convened at NBS.

The Metallurgy Division's programs also include direct contributions to industry through the NBS Research Associate Program. Extensive interaction with universities exists through the Cooperative Education Program, NBS Postdoctoral Program, and faculty guest workers. Considerable interaction also exists with other Government agencies, standards organizations, and the technical community at large. For example, the Division performs research for the following Government agencies: the National Aeronautics and Space Administration, the Office of Naval Research, the Defense Advanced Research Projects Agency (DARPA), the Department of Energy (DOE), the Naval Ship Research and Development Center, and the U.S. Army Materials and Mechanics Research Center.

## STRUCTURE CHARACTERIZATION

Task 12142 and

## SYNCHROTRON RADIATION RESEARCH FOR MATERIALS SCIENCE

Task 51105

Innovative processing techniques are being developed to produce significant new microstructures and structural/property relationships. Coupled with increased industrial emphasis on quality control and automation, these advances require a wide range of microstructural characterization and nondestructive evaluation methods. The objectives of this task are to address this challenge through the development of measurement methods (including nondestructive techniques) and standards for the advanced quantitative characterization of metallurgical microstructures. These developments would permit automatic control methods for manufacturing and in-service use of industrial alloys. Methodologies include x-ray, optical and electron microscopy, eddy current, magnetic particles, electrical conductivity, acoustic emission, and ultrasonic methods.

A new competence program in Synchrotron Radiation was initiated in FY80 as a part of this task. The availability of intense, tunable, well-collimated radiation at synchrotron radiation facilities will permit radical gains in experimental and theoretical materials science. As a joint NBS/NRL effort, we aim to establish an x-ray instrumentation complex at the NSLS and to use it to perform frontier experiments in transformations in materials, kinetic studies, furtherance of x-ray optics, and the study of inner shell dynamics. One intermediate-term goal of this effort is to establish an advanced x-ray analysis capability at BNL and to apply this to the topographic analysis of cracks in a stressed metal alloy and to glass-crystal metal alloy transitions.

As part of our FY82 Metals Processing Initiative, new laboratory facilities were established for quantitative microscopy, ultrasonic scattering, and acoustic emission. In the microscopy area, a TEM and a Quantimet have been added, and a SEM is upgraded with energy dispersion spectroscopy (EDEX). In the NDE area, new capabilities such as an interferometer, a computer, and other new ultrasonic equipment were added.

This group's accomplishments in FY82 are in two major areas:

1. A competence program of the application of synchrotron radiation to materials science, in which this group in the Metallurgy Division is taking a lead in the construction of hard radiation ( $0.5 \text{ \AA}$  to  $5 \text{ \AA}$ ) branch lines at the NSLS in BNL for CMS and NRL scientists to perform unique experiments for research problems in materials science.
  2. A new initiative for metals processing, where our group's effort lies in the improvement of microstructure characterization facilities.
- The assembly of the CMS Synchrotron Radiation Beam Lines at NSLS in BNL, which include two monochromator tanks, two hutches (experimental stations for small angle scattering and real-time topography), and beam transport mechanisms.



- The establishment of a new x-ray analysis capability in one of our scanning electron microscopes as part of the new initiative effort for metals processes.
- The establishment of a new four megabyte capacity minicomputer for analysis of varieties of data ranging from acoustic emission signals to predictive modeling computation of phase diagrams.
- The establishment of a new laser interferometry for microstructure characterization by acoustic emission.
- The establishment of white radiation topography techniques and an initial application to the characterization of Czochralski grown Fe-Al crystals, Ni crystals, Al and Sn powders, Al polycrystals, NaCl crystals, electron beam melted Si crystals, Al<sub>2</sub>O<sub>3</sub>, 2024 Al, and human teeth.
- The development of second generation charged-couple-device image intensifiers for real-time topography.
- The routine operation of in-house focused EXAFS and SEXAFS for various amorphous materials such as metallic glasses and ultra-thin passive films on metals and alloys.

Other programmatic goals of this task are to quantitatively evaluate acoustic emission in steels and aluminum alloys and to compare the data with theory, and also to develop ultrasonic spectroscopy so that it can be effectively used in microstructural characterization and quality control of defects during the processing and use of structure alloys.

Another effort includes both the microstructure characterization studies through ultrasonic measurements and the monitoring of melting and solidification events during surface modification by AE. Other efforts are aimed at developing new eddy current standards and electrical conductivity measurements, and in placing established techniques such as the magnetic particle method on a more quantitative and reproducible basis. The National Measurement Laboratory (NML)-Scanning Electron Microscope facility is also located in this task. This facility not only serves on-going research efforts, but is also used in the development of standard reference materials for SEM.

In connection with our program objectives, the Metallurgy Division has sponsored a workshop on process control sensors for the steel industry jointly with the American Iron and Steel Institute and the Defense Advanced Research Projects Agency. The aim of this Briefing/ Workshop is to first provide industry, university, and Government scientists and engineers with the specific Process Control Sensor needs of the steel industry; and secondly, to seek immediate input and future research and development involvement from a broad spectrum of disciplines to facilitate development of the sensors.

Finally, new programs were initiated in coupling of the nondestructive evaluation program to rapid solidification processes as well as cooperation with The Johns Hopkins University and University of Maryland. In

association with the rapid solidification process program, a new contract was established with DARPA.

Under this competence program which started in FY80 and a new initiative, research collaboration was established with many scientists. Simon C. Moss, Professor of Physics, University of Houston, has remained as consultant for this year. Through the U.S./France International Cooperative Program of Materials Science, Z. Baran, Professor of Physics, University of Paris V, has joined our group as a guest worker. This program for synchrotron/x-ray topography was initiated in 1980 (see 1980 Annual Report) by the participation of an NBS scientist in collaboration with the National Science Foundation. We have maintained close collaboration with Professor Haydn Chen, University of Illinois; Professor Ronald W. Armstrong, University of Maryland; Professor Robert E. Green, Jr., The Johns Hopkins University; Professor Barton Roessler, Brown University; Professor Yi-Han Kao and Mr. Allan Goldman, State University of New York (Stony Brook); and Dr. K. C. Yoo, Guest Worker from the University of Maryland; to perform experiments. Several international collaborations have been maintained and initiated and others have been with Professor H. J. Queisser and Dr. W. Hartmann, Max-Planck Institut fur Festkorperforschung, Stuttgart, Germany; Professor G. Hildebrandt, Fritz-Haber Institut der Max-Planck Gesellschaft, Berlin, Germany; Dr. J. Chikawa, Broadcasting Science Technology Laboratories, NHK, (Japan Broadcasting Corporation) Japan; and Professor T. Imura, Nagoya University, Japan; on the development of real-time imaging in x-ray topography. Two distinguished visiting scientists were actively involved in the activities of this task during FY82. They were: Dr. M. Rosen of Ben Gurion University, Israel, and The Johns Hopkins University, Baltimore, MD, and Dr. H. N. G. Wadley of the Atomic Energy Research Establishment, Harwell, England.

The task is divided into subtasks whose activities and accomplishments over the past year are described next.

#### Synchrotron Radiation Research for Materials Science Task 51105, and

#### Application of Synchrotron Radiation to Material Science Subtask 1 of Task 12142

M. Kuriyama, W. J. Boettinger, G. G. Cohen, R. C. Dobbyn, R. D. Spal, and H. E. Burdette

As the Center for Materials Science's part of the NBS/NRL synchrotron radiation research program at the NSLS, a group in the Metallurgy Division has taken a lead in the construction of hard radiation (0.5 Å to 5 Å) branch lines so that CMS and NRL scientists can make use of unique synchrotron radiation characteristics, such as high flux and tunability, for research problems in materials science. The beam lines include facilities for real-time topography, small angle scattering, interface/inelastic scattering spectroscopy, and crystallography. Scientific problems are aimed at advancing materials science by utilizing techniques which were previously impractical. For example, the high flux in the synchrotron beam makes possible the observation of local phenomena in materials in



real-time. The energy and momentum resolution can be made extremely good so as to increase the precision in the determination of the atomic coordination and arrangement. Furthermore, the tunability of the radiation for the desired energy band pass enables us to focus on a particular atomic species (elemental tunability) for the precise determination of behavior under the influence of neighboring atoms in different local volumes. The ultimate goal in materials science would be the formation and verification of discrete atomistic theory for rates of phase transformation and structure stability. In approaching this goal, we have placed an emphasis in the initial phase, on the development of dynamic in situ measurement capability to obtain an advanced knowledge on the kinetics of microstructural transformations, and investigations of short- and long-range order in various local volumes.

For the development of our synchrotron radiation beam lines at NSLS, simultaneous activities are required in the four areas: (1) overall beam line design; (2) new x-ray diffraction configuration, including the development of prototype instruments; (3) monochromator/experiment designs; and (4) computer control. Our basic philosophy for the CMS experiments is to deliver x-ray monochromatic photons of energies between 5 keV and 30 keV by the simplest method and to create a high degree of energy, momentum, and spatial resolution, primarily through flat crystal diffraction optics. The beam is to be transported through Be windows (10 to 15 mils thick) in an atmosphere of He. During the past 2.5 years, we succeeded in achieving all goals in these four areas with the aid of both a 12 kW high intensity rotating anode x-ray source and a synchrotron radiation source at Cornell University (CHESS). We have entered into Phase III, in which scientists are now working more frequently and regularly at NSLS than at NBS.

A trailer has been purchased at the site of NSLS to be used as a small lab for the preparation of our experiments at the beam lines. This trailer is necessary because there is not enough working space in the beam line area. We have also established an account at NSLS to cover costs associated with setting up the beam lines and performing experiments. Two monochromator tanks and a beam transport port, which were constructed by the NBS machine shops, are now being assembled at NSLS and being connected to experimental hutches. The CMS synchrotron radiation beam lines will be completed by the end of summer upon the completion of the front end, which will be provided by NSLS.

To make the synchrotron radiation activity more effective, we have carried out several experiments, independent of the beam line construction using our in-house EXAFS experimental capability and CHESS synchrotron radiation. Our in-house EXAFS experimental capability, which was established through our prototype development for the synchrotron radiation program, is now in routine operation. This capability, unique in the field of EXAFS, features automatic focusing with tunable energies of the incident x-ray beam from 5 keV to 25 keV. This system is completely computer controlled and data are analyzed automatically on site. This new system has stimulated interest among many scientists; we are now performing EXAFS experiments on catalysts, layered thin films, oxides, surfaces of thin films, Ti-compounds, metallic glasses, and biological



samples with Dr. D. Peterson, Dow Corning; D. Denley, Shell; W. Gibson, SUNY/Albany; W. Wagner, Bell Laboratories; and Y. H. Kao, SUNY/Stony Brook. This in-house EXAFS system has also been used by NBS scientists in other centers in collaboration with us. The EXAFS technical activities in our Division are described later. Using synchrotron radiation at CHESS, we have explored a white radiation topography technique on both a stationary and a real-time basis, and we have applied it to various real materials including industrial alloys and human teeth (collaboration with the American Dental Association). We have also performed monochromatic radiation topography as developed in the past years [1,2] (See 1981 Annual Report) and made an initial effort of establishing quantitative microstructure characterization involving detailed structural modeling or the mapping of strains within a sample.

To summarize the present status in this CMS synchrotron radiation program, we have begun assembling beam transport, experimental hutches, and monochromators at NSLS. Our prototype experiments for testing new x-ray optical methodology have now been expanded to develop methods for the future application to quantitative microstructure characterization. In connection with these activities, we were invited to write a review article on synchrotron radiation topography for the Annual Review of Materials Science [3]. Some highlights of our technical activities in the CMS synchrotron radiation materials science program are described later in more detail.

- [1] Kuriyama, M.; Boettinger, W. J. Application of synchrotron radiation to materials science. Annual Materials Research Society Meeting, Boston, MA. 1981, November 16-19.
- [2] Boettinger, W. J.; Dobbryn, R. C.; Burdette, H. E.; Kuriyama, M. Real-time topography with x-ray image magnification. Nucl. Instrum. Methods, 195: 355; 1982.
- [3] Kuriyama, M.; Boettinger, W. J.; Cohen, G. G. Synchrotron radiation topography. Annu. Rev. Mater. Sci. 12: 23; 1982.

Initial Development of Real-Time White Radiation Topography  
Subtask 2 of Task 12142

W. J. Boettinger, H. E. Burdette, R. C. Dobbryn, and M. Kuriyama

X-ray topography is a nondestructive technique to image certain types of metallurgical and ceramic microstructure from the surface or through the thickness of samples under Bragg diffraction conditions. Depending on the wavelength of the radiation and/or the perfection of the crystalline samples, the depth of material observed can range between 1  $\mu\text{m}$  and 1 mm. Topographs are obtained for the detailed interpretation of images produced by x-ray diffraction by real crystals. There are many situations, however, where such a detailed study is neither required nor possible. Because of the wide variety of materials and microstructures of interest in materials science, a simple and rapid method for data collection is desirable. One such method is white radiation (Laue) topography, which is particularly suited to the early detection of a crystal grain newly formed from the melt.

The direction and magnitude of dislocation vectors, or the determination of active slip systems can readily be obtained from a Laue pattern containing different diffracting planes simultaneously.

White beam synchrotron topography requires only three optical elements: the source, the sample, and the detector. The method is the same as the Laue reflection or transmission methods commonly used for crystal orientation. The sample is placed in the white synchrotron beam and a Laue pattern is recorded either on film or on a phosphor (for real-time observation) viewed by a TV camera.

Each Laue spot contains the fine structure of a topograph as shown in figure 1. Grains of arbitrary orientation are imaged because the sample itself selects the appropriate wavelength to locally satisfy the Bragg condition. Accurate positioning and orientation alignment are not required. There is no need for scanning, and data can be obtained from several Laue spots simultaneously yielding information at different x-ray wavelengths. Of course, there are serious shortcomings in this technique. However, depending upon the microstructures of interest, this is the easiest technique to implement. (In terms of defect analysis, however, it is probably the most complex.)

We have applied this technique, using synchrotron radiation at CHESS, to various materials for different objectives [4]. A typical synchrotron radiation white beam Laue photograph (a set of topographs) is shown in figure 1, which was taken from a Czochralski-grown Ni crystal in the transmission geometry. This crystal contains several subgrains. At a quick glance it is easily recognized that the position of the oval shaped subgrain in various Laue spots shifts around the central spot, indicating the orientation (rotation) of this subgrain relative to the major grain. This demonstrates a typical merit of white beam topography for a quick and over-all assessment of microstructures. Even residual stress effects can easily be detected as shown in figure 2. This is a Laue set of synchrotron white beam transmission topographs of a Si crystal, which contains a spot created by an electron beam on the (111) surface. This spot was melted by the electron beam and resolidified. The residual stress pattern extends outward from the weld spot.

Another benefit of synchrotron white beam topography is the applicability to almost any sort of solid, including industrial materials, as shown in figures 3 and 4. Figure 3 shows a few examples of topographs obtained from Laue spots of an Al powder. Al powder particles were solidified with large undercooling, which made each particle single crystal-like. These topographs immediately indicate whether these particles are a single crystal with a single nucleus or two grains. Also, information is obtained as to whether these grains are deformed by strains, although particle shapes are visibly spherical. Figure 4 demonstrates microstructures in a so-called single crystal turbine blade.

An enlarged view of a white beam topograph, figure 5, of a Fe 24 at. % Al alloy shows dumb bell images of inclusions. These inclusions are not visible optically. This topograph also indicates the existence of other imperfections, prompting a more detailed study of this crystal by monochromatic radiation topography, as shown in figure 6. This is a typical



representation of the effective use of white radiation topography; that is, it is a rapid assessment of crystal microstructure leading to a more detailed research.

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Quantitative Analysis of Strains Within a Crystal by Monochromatic Radiation Topography  
Subtask 3 of Task 12142

K. C. Yoo, R. C. Dobbyn, and M. Kuriyama

The work hardening which occurs at hardness impressions is considered to be a major factor in determining the microhardness properties of single crystals or of individual grains within polycrystalline materials. For example, the orientation dependence of the crystal work hardening determines the level of microhardness pressure and hardness anisotropy which is measured for different directions of the indenter axes of Knoop or diamond pyramid impressions. The pressure and anisotropy are critically dependent on how a particular set of slip systems is activated by microhardness indentations.

As an initial attempt to develop a quantitative method of analyzing local strains within a crystal by x-ray topography, we employed a real time topographic system previously developed [5] (See 1981 Annual Report) with a second generation image intensifier (See 1982 NDE Annual Report) to the characterization of hardness indentations in a NaCl crystal and a copper crystal, using synchrotron radiation at CHESS.

First, we have demonstrated the possibility of observing in a continuous way how these slip systems develop on a real time basis. Secondly, we obtained a series of topographs as a function of x-ray glancing angle, while the whole sequence was recorded on a video tape, to confirm the prediction of image contrast inversion [6]. This kind of experiment has been impractical or impossible with laboratory x-ray sources. Figure 7 shows x-ray optical arrangement for changing glancing angle  $\theta_{in}$  as well as an  $04\bar{4}$  topograph of NaCl at  $\theta_{in} = \text{Bragg angle}$ . Images around indentation impressions were analyzed in a similar fashion to a previous work on Cu [7] for the determination of active slip systems and slip directions.

We also obtained a series of topographs from a Cu crystal with Knoop indentations as a function of  $\theta_{in}$  as well as  $\theta_{out}$  (observation angle), as shown in figure 8. This set of topographs is required for detailed (quantitative) information on strains associated with indentation impressions. Without synchrotron radiation, it is impossible to obtain such a series within a realistic time frame. This approach, in a general line broadening context, opens up a new avenue of characterizing imperfections locally and quantitatively in terms of dynamic structure factor which contains local atomic displacements.



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- [6] Kuriyama, M.; Cohen, G. G. Z. Naturforsch 37a: ; 1982; in press.
- [7] Yoo, K. C.; Roessler, B.; Armstrong, R. W.; Kuriyama, M. Scr. Metall. 15: 1245; 1981.

Structure of Nickel-Phosphorus Metallic Glasses  
Subtask 4 of Task 12142

G. G. Cohen, M. Kuriyama, and A. J. Goldman

Fourier transforms of EXAFS data have been used to study the positions of atoms surrounding the Ni atoms in glassy Ni-P. The structural analysis, which was carried out as a function of processing parameters, was used to show that at least two local configurations exist for a given metal-to-metalloid composition.

When amorphous alloys are annealed far below the crystallization temperature, structural changes (i.e., "relaxation") and concomitant changes in density are often seen. This process is probably continuous in some cases [8]. The present measurements, however, indicate that in the Ni-P case, at least two metastable states exist for a single composition.

EXAFS spectra have been obtained for dc plated and pulse plated glassy  $\text{Ni}_{75}\text{P}_{25}$  samples and for polycrystalline  $\text{Ni}_3\text{P}$  powder, as well as for pure Ni foils. Backscattering amplitudes and phases were determined for Ni-to-Ni and Ni-to-P using the latter two samples as standards. Theoretical curves were also obtained using parameters obtained (or interpolated) from Teo et al. These calculated curves indicated that the measured spectra are dominated by the Ni to P distances, and were used to demonstrate that the pulse plated sample distances were stretched by 0.01Å as compared to the crystalline  $\text{Ni}_3\text{P}$  and the dc plated samples (which were the same within experimental error).

These results are in agreement with recent Mössbauer measurements [9] on similar samples and with published density results. However, none of the earlier methods could probe the radial distances directly, and that has been accomplished here. The EXAFS results can be taken as complementary to the other techniques, and as adding a new dimension to structure determination in amorphous materials.

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- [9] Lashmore, D. S.; Bennett, L. H.; Schone, H. E.; Gustafson, P.; Watson, R. E. Polymorphism of nickel-phosphorus metallic glasses. Phys. Rev. Lett. 48: 1760; 1982.

Structural Study of Passive Films on Iron  
Subtask 5 of Task 12142

G. G. Cohen, D. R. Black, and M. Kuriyama

The first application of the surface EXAFS (extended x-ray absorption fine structure) technique to the structure of thin ( $< 3$  nm) passive films on iron was carried out in a joint effort between the Materials Chemistry and the Metallurgy Divisions of CMS.

The samples were 50 Å thick vapor-deposited Fe films on glass, which were passivated by either a chromate or a nitrite passivating solution. Near edge and extended x-ray absorption fine structure spectra were measured on these films, as well as, on bulk Fe, and on an air-exposed film.

The energy position of the K-edge discontinuity of a material is a function of the effective charge and the electronic configuration of the absorbing atom. The edge shift of the chromate-formed film was 5 eV lower than either the nitrite-formed film or the air-formed film (which were within 2 eV of each other). This indicates a significantly lower coordination charge for the chromate-formed film and a likely greater covalency in the bonding of the iron in this film.

The K-edge discontinuity is sometimes accompanied by a "white line," or a strong enhancement of the absorption coefficient, in the region within 50 eV of the edge. The white lines indicate an empty or partially empty state of p-character near the edge, which can be traced to the formation of excitation levels or to a high density of states embedded in the continuum. As is usual for a transition metal element, there is no white line in the K-absorption spectrum for Fe metal. Enhancements in the absorption coefficient are clearly visible in the nitrite-formed and in the air formed films, but are suppressed in the chromate-formed film (fig. 9).

The EXAFS data was Fourier transformed to obtain the radial distances about the Fe site. A comparison of the first neighbor and the second neighbor coordination shells can be used as a measure of "the relative disorder in a material." It was found that the air-formed film exhibited the most order (crystallinity) and the chromate-formed film the most disorder, while the nitrite-formed film was intermediate between the two. This suggests that the passive layers in the chromate-formed film are arranged in a more glass-like structure about the Fe atoms. The Fourier transform of the chromate-formed film data is shown in figure 10.

Attempts were made to examine the structure around the Cr atom in the chromate-formed film since many workers have found Cr in such films. A lower limit of at least 12 percent Cr was found in the film, and an analysis of the structure is underway.

It is intended to study the breakdown of passivation next, and therefore we also examined a chromate-formed film that had been exposed to a chloride solution for about one hour. Although no change was seen in the position and shape of the K-edge for this sample, the same alteration in the radial distances can be detected at this level.



Earlier attempts to determine the nature and structure of the passive film on Fe, such as electron microscopy, Auger, and ultraviolet photo-emission spectroscopy, have required ex situ examination of the passive layer in a vacuum environment. This environment could alter the structure of the film by, for example, removing water from the samples. The work described above provides structural and compositional information on the passive film in a non-vacuum environment, and also yields information on the electronic configuration about the metal site.

#### Development of a Surface EXAFS Chamber and a High Resolution Analysis Technique

Subtask 6 of Task 12142

G. G. Cohen and D. R. Black

Following along the lines suggested by Fischer and Shevchik [10] a band-pass ionization chamber surface-EXAFS chamber was built, and is undergoing further development [11]. This surface chamber operates with the sample in an He environment and serves to collect the fluorescence signal over a full hemisphere ( $2\pi$  steradians). It is estimated that more than an order of magnitude is gained in sensitivity through the use of this device. It currently is computer controlled, operating through a high sensitivity picoammeter and rapid A-to-D converter. We estimate the lower limit of sensitivity to be a  $10 \text{ \AA}$  film, limited by the present level of signal-to-noise. Samples of metallic glasses of FeB and FePC were first measured with this device, and the results compared to P diffusion data from the same samples. A high-resolution curve fitting technique was developed to study the second-neighbor shoulder with good resolution in the Fourier transform. Until now, few EXAFS studies in the literature can resolve the higher order coordination, which is now routine in this laboratory.

[10] Shevchik, N. J.; Fischer, D. A. Rev. Sci. Instrum. 50: 577; 1979.

[11] Fischer, D. A.; Cohen, G. G.; Shevchik, N. J. J. Phys. F 10: L139; 1980.

#### Scanning Electron Microscope

Subtask 7 of Task 12142

D. Ballard

We continued the service and maintenance of the NML-SEM facility and support equipment to satisfy the needs of NML personnel for electron microstructure examination of materials involved in research activities at NBS. Thirty-six hours of individual instruction on the operation and techniques of scanning electron microscopy were provided to five NML personnel.

The SEM was used to measure the diagonal indent length on Micro Hardness Conversion Blocks of a round robin test sponsored by ASTM E04.05. The measurements were made on SEM photographs whose magnification was accurately calibrated by use of the NBS-SRM 484 (SEM magnification standard). In



addition, a review of the Knoop indent images indicated that for best overall illumination, the long axis of the indent should be perpendicular to the SEM scintillator axis and at 0 tilt with respect to the 10 kV electron gun beam. The increased resolution of the SEM above that of the optical microscope revealed defects within the indents that could lead to erroneous values particularly for the 25 g loads, i.e., specimen porosity, polishing scratches, diamond surface defects, and off-axis indent impressions.

The last sample of SRM-484b was issued to fill orders received prior to April 1982. At the present time, OSRM has 16 requests on back order. Work has begun on the next issue of 150 units designated SRM-484c. Present plans include calibration of the new units by use of a high resolution SEM under computer control and a laser interferometer measurement output system. Use of this instrument, located in the Mechanical Production Metrology Division, should provide improved accuracy and shorter turn-around time for unit calibration. The SRM-484 is now referred to in part of MIL Specification # 883-B as the control standard used in the measurement of integrated circuits by the SEM.

Several different carbon fibers were investigated in an effort to satisfy the specimen criteria necessary for application of the proposed ASTM Standard Practice for SEM Performance Characterization. The results of observation on some of the carbon fibers will be presented and published in the EMSA Proceedings 1982, Sputter Coated Carbon Specimens for SEM Performance Testing, by D. R. Black and D. B. Ballard.

The basis of the performance test is to measure the horizontal offset of a recorded waveform produced as the electron beam scans across a well-defined edge of a suitable material. The resultant waveform is a product of the electron beam parameters and its interaction with the specimen. A low Z element such as carbon may not be the optimum material due to electron beam spread and penetration. In view of this, several metals and edge preparation techniques are being studied as possible candidates for production of a satisfactory SRM.

Part of the investigation of the Kansas City Hyatt Regency Walkway Collapse included SEM fractographic analysis of the failed weld areas of the fabricated box beams and fractured washers of the suspension structure. The result of the SEM fractographic analysis was included in NBSIR-82-2465 report.

#### Contactless Laser Generation and Optical Interferometric Detection of Ultrasonic Waves

##### Subtask 8 of Task 12142

H. N. G. Wadley, M. Rosen, S. Fick, F. Nadeau, and R. Mehrabian

Transient loads applied by rapid energy transfer from a single-pulse Q-switched high-energy laser generate compressive stress waves that propagate in a material. Propagation of ultrasonic waves in a medium cause surface displacements that can be measured optically by exploiting the phase shift of an optical beam reflected from the surface of the material. When the reflected beam is approximately combined with a

reference optical beam, from a helium-neon laser, phase changes are converted into amplitude changes, detectable by a suitable photodiode. These amplitude changes are proportional to the surface displacements on the specimen. Potential problems arising from the fact that phase changes also result from relative motion among the optical components of the system, and even from fluctuations of the ambient air, are avoided by appropriate features in the mechanical design of an interferometer. An arrangement due to Fizeau is inherently compact and mechanically stable, and thus well-suited to the present application. Two such Fizeau interferometers can readily be combined so that the two optical probes may be separated by a convenient distance to allow accurate measurement of the travel time of an ultrasonic wave in the specimen over a well-defined distance. Furthermore, the variation in magnitude of the surface displacements detected by the two Fizeau interferometers determines the ultrasonic attenuation in the specimen. This specific system with dual Fizeau interferometers allows the simultaneous determination of both elastic-wave velocity and ultrasonic attenuation.

Compared with other sensors, interferometers offer several advantages. The sensitive area is definite, and can be made as small as a few microns in diameter for highly localized measurements. A known quantity, displacement, is measured; independent methods of absolute calibration are applicable which give small overall errors. Bandwidth, determining the fidelity of reproduction of signal waveshapes, is limited not by the physical nature of the transduction process but by its associated electronics. In this respect, performance can exceed that of conventional piezoelectric transducers. Small signal resolution and bandwidth are related; displacements of a few angstroms are detectable at 7 MHz bandwidth. Laser loading produces a stress pulse of high amplitude and short duration so that investigation of highly attenuating, or very thin, specimens is possible. The noncontact feature of both generation and detection of ultrasonic waves is advantageous in situations requiring physical separation between the measuring system and the specimen. Furthermore, the noncontact mode of generation and detections precludes interaction with, and modification of, the wave propagation under study.

The two-channel, quadrature-dual laser interferometer developed and constructed permits highly accurate sound wave velocity measurements of longitudinal, transverse, and Rayleigh waves. From the absolute surface displacement measurements, it is possible to determine the values of the attenuation of these waves, as well as, their frequency dependence.

The contactless method of generation and detection of ultrasonic waves permits dynamic measurements to be performed whereby the specimen is subjected to programmed heat treatments, or is positioned in a hostile atmosphere. The noncontact mode of generation and detection precludes interaction or modification of the wave propagation under investigation. This unique dual-channel laser interferometer is in the process of final adjustment and calibration.



NDE Characterization of Thin Structurally Modified Surface Layers on Bulk Substrates  
Subtask 9 of Task 12142

M. Rosen, F. Nadeau, and R. Mehrabian

Laser and electron beam irradiation techniques are being applied extensively for the modification of properties of the surfaces of metallic structures. High intensity power transferred onto the metallic surface produces a liquid pool that rapidly solidifies under the influence of the chilling effect of the cold substrate. Formation of hard martensitic layers, soft pearlitic bulk, solid solution strengthening of the peripheral layer, grain size refinement, dispersion hardening, or formation of an amorphous layer on a crystalline substrate can be achieved by laser or electron beam heating. Of particular interest, from both technological and scientific points of view, are the physical and mechanical properties of the modified surface layer, as well as its dimensions. In most instances, the thickness of the modified layer is not accessible to nondestructive testing. However, the determination of the thickness of a case-hardened steel shaft may be of prime importance for engineering design. Similarly, in the case of amorphous glazing of a crystalline substrate. The physical properties of the amorphous layer and its depth may be important parameters for the evaluation of the efficiency of the glazing process and determination of the strength of the modified layer.

Microstructural modifications in peripheral layers of bulk specimens was obtained by means of rapid heating and cooling with an electron beam. Relatively thick amorphous layers (about 1 mm) were obtained on crystalline PdCuSi. In addition, martensitic and bainitic microstructures were produced on pearlitic steel plates. The NDE characterization is being made by measuring the Rayleigh surface wave velocity. Therefore the metallurgical characteristics and the thickness of the modified layer can nondestructively be determined.

The essence of this research was to develop a technique by which Rayleigh surface waves may be launched. The Rayleigh waves propagate within the surface layer only or penetrate the substrate depending on the wave frequency. The Fourier analysis of the frequency content of the Rayleigh waves allows determination of the thickness of the layer provided its elastic moduli differ by several percent from those of the crystalline substrate.

Crystallization Kinetics Study of Amorphous Zr-Cu by Ultrasonic and Microhardness Measurements  
Subtask 10 of Task 12142

M. Rosen, F. Nadeau, and R. Mehrabian

Metallic glass formation and subsequent crystallization upon heating has recently become an active research area. Rapidly solidified amorphous alloys exhibit a variety of desirable physical, chemical, and mechanical properties that are particularly attractive for products in electronics and power industries. Moreover, functional and economic advantages may



be gained when crystallizing specific alloys into microcrystalline structures that can be subsequently consolidated into bulk products. Microstructural characterization using nondestructive techniques, e.g., ultrasonics, may thus be attractive both for its contribution to understanding the kinetics and mechanism of the transformation and for its ultimate application for on-line feedback control of materials processing variables.

Metallic glasses are not thermodynamically stable, and they tend to structurally relax and finally crystallize upon appropriate heat treatment. The activation energy for relaxation continuously increases with time, which may correspond to the removal of quenched-in defects. Associated with relaxation and crystallization are variations in the elastic and mechanical properties. Young's modulus  $E$  and shear stiffness  $m$  generally increase by 20 to 40 percent, but the bulk modulus  $K$  by only about 7 percent upon crystallization. The density of glassy metals is generally only 0.3 to 1.5 percent less than the corresponding crystalline structures. As-quenched glasses contract approximately 0.5 vol % during relaxation.

Straightforward elasticity and wave propagation theories enable one to calculate Young's modulus  $E$ . For one-dimensional extensional wave propagation in a homogeneous, isotropic, linearly elastic solid. Young's modulus is given by  $E = \rho v_E^2$  where  $v_E$  is the extensional wave velocity and  $\rho$  is density.

The Cu-Zr metallic glass ribbons were prepared using the melt-spinning technique. A 2 mm wide, 30 mm thick ribbon was produced. Ultrasonic, x-ray and STEM examinations indicated that the ribbon was completely amorphous. The ribbons were heat treated in evacuated capsules at temperatures above the glass transition point,  $T_g$ , for different time intervals in order to obtain information about the crystallization kinetics and its mechanism.

The objective of the present investigation was to study the crystallization kinetics of Zr-Cu ribbons (about 50  $\mu\text{m}$  in thickness) by means of laser-generated and piezoelectrically detected, ultrasonic waves whereby the extensional wave velocity, and consequently the Young's moduli could be determined as a function of crystallization time. The amorphous-to-crystalline kinetics could thus be determined to a high degree of accuracy.

The inherent difficulty of measuring sound-wave velocities in thin-ribbons was overcome by developing a technique applying the load on the specimen by means of rapid deposition of energy from a single-pulse of a Q-switched Nd:YAG laser. A state of unbalanced compressive thermal stress is produced. The stress gradient propagates along the ribbon in the form of an elastic wave. The piezoelectric crystal, at a distance from the spot where the laser radiation was deposited, detects the local displacement. Thus, the transit time of the propagating wave could be determined accurately by means of a transient-pulse recorder. In this work, ultrasonic extensional waves were detected using a National Bureau of Standards conical PZT transducer having a flat response between dc and 2 MHz. Signal amplification was provided by an EMI 6306 charge-sensitive amplifier powered by an EMI Power Supply Type 6396. A silicon photodiode triggered a Nicolet Explorer III digital oscilloscope so that the elastic wave

could be recorded and transit times read directly from the screen of the oscilloscope. The transit times were determined to be better than 1 part in  $10^4$ , and the source-receiver distance to within +0.3 percent. All velocity measurements were conducted at room temperature.

Small sections of each heat treated specimen were mounted in epoxy for Knoop microhardness number (KHN) measurements. To minimize anvil effects and to ensure that KHN values were taken of the bulk material, each specimen was cut perpendicular to its length vector, and then was mounted with its cut face exposed. After polishing the mounted ribbons to 0.05  $\mu\text{m}$  alumina, KHN values were determined using a 10 g load and averaging four symmetrical indentations.

The structural relaxation and crystallization effects induced by isothermal heat treatment on the room temperature ultrasonic extensional wave velocity, Youngs' modulus, and Knoop microhardness of Cu-Zr ribbons are summarized below.

Velocity versus log-time curves exhibited isokinetic sigmoidal behavior. Extensional wave velocity increased  $\sim 2.0$  percent and Young's modulus by 4.0 percent due to structural relaxation. Young's modulus increased 43 percent upon transformation from the amorphous to the fully crystalline state. Knoop microhardness increased to a relative maximum, equal to 44 to 88 percent of the asymptotic KHN value, during structural relaxation. KHN then decreased to a minimum, due to stress relief annealing. The final microhardness rise to an asymptotic KHN value of  $\sim 720 \text{ kg. mm}^{-2}$  was due to crystallization of a hard, brittle equilibrium CuZr phase.

Using data derived from the velocity versus log-time curves, the activation energy for 50 percent crystallization was found to be  $360 \text{ kJ mol}^{-1}$  and the  $n$  parameter from the Johnson-Mehl-Avrami equation was approximately unity. This value is consistent with one-dimensional diffusion-controlled growth.

An as-spun ribbon contains many quenched-in defects so that the glass may be viewed as having a continuous distribution of varying coordination or excess free volume. Reduced coordination in given atom complexes permits the material to undergo shear transformations without undue constraint and results in a ductile metallic glass. Heat treatment removes quenched-in excess free volume through structural relaxation. The amorphous material thus approaches the ideal glassy state, having a rigid close-packed atomic distribution. Consequently, the glass should harden and become less ductile in the relaxation regime. This behavior was indeed observed in the present study. The main contribution to hardness was attained during the relaxation of the amorphous phase.

#### Eddy Current Standards Subtask 11 of Task 12142

##### A. J. McAlister

The eddy current method is widely used in both the ferrous and nonferrous metals industries for nondestructive detection of flaws such as cracks, inclusions, and variations in composition and microstructure in metals



and metal parts via local changes in electrical conductivity. Primary conductivity standards are needed for reliable execution of this work, but to date, this need has been supplied by industry itself. The necessary range of conductivity for industrial testing is from 0.585 to 58.5  $\text{MSm}^{-1}$  (1 to 100 percent IACS).

The properties desired in a primary conductivity standard are long term stability, durability, and low magnetic susceptibility. (In testing of high susceptibility steels, normal practice has been to apply a saturating magnetic field to reduce the differential permeability to a value near that of vacuum.) Hence, elemental metals and alloys of equilibrium phase composition, upon which stable nonconducting surface layers can be formed, are desirable. The surface properties are important not only for durability, but for reproducible lift-off behavior as well.

Our overall aim is the selection of metals and alloys suitable for primary conductivity reference standards, and the preparation of specifications for their preparation and fabrication. Progress to date in this work is summarized in the following table, in which target conductivity, material, condition of the material as examined, observed conductivity and its extreme variation over the sample faces, and status of the material are listed.

Summary of Conductivity Testing

Target Conductivity (% IACS)	Material (w/o)	Status	Condition	Observed Conductivity and range (% IACS)
101	OFHC Cu	*	annealed	101.9 + 0.1
		*	unannealed	99.5 + 0.2
85	1.3 Zn + Cu	#	as cast	81.1 + 0.4
75	2.4 Zn + Cu	#	as cast	70.4 + 0.4
60	Al 1100F	+	complete	60.0 + 0.05
48	Al 2024-0	+	complete	47.0 + 0.1
41.5	Al 6061-T	+	complete	41.0 + 0.05
29	Al 2024-T-351	+	complete	30.0 + 0.1
23	21.5 Zn, 2.5 Al + Cu	#	as cast	20.5 + 0.3
17	7 Al + Cu	#	as cast	15.6 + 0.1
17	6 Ni + Cu	*	as received	17.7 + 0.1
12	1.5 Si + Cu	#	as cast	10.1 + 0.2
7	3 Si + Cu	#	as cast	7.5 + 0.2
7	23 Ni + Cu	*	as received	6.11 + 0.01
3.5	Ti, Grade 4	*	unannealed	1.95 + 0.05
3.5	45 Ni + Cu	*	as received	3.440 + 0.002
1.0	8 Al, 1 Mo, IV + Ti	*	unannealed	1.07 + 0.007 0.86 + 0.012
1.0	6 Al, 4 V + Ti	*	unannealed	0.97 + 0.005

Status is indicated as: +, finished, calibrated standards; \*, commercial products, faced and examined; #, alloys cast in-house, faced and examined.

Production and calibration of the Al-based standards is complete.



Apparent conductivity variation over the surfaces of commercial alloys appears random, and is taken to reflect the variation to be expected in as received condition. The better uniformity of annealed vs unannealed Cu is due to the removal of cold work damage. Annealing did not improve Ti or the Ti-based alloys. The major part of the conductivity variation in the as cast Cu-based alloys is due to solute segregation upon solidification, and should be largely removed by homogenization.

The decision to focus on Cu-based alloys outside the Al and Ti ranges, and to prepare special melts, was not made lightly. As a practical matter, it is essential that the magnetic permeability of an eddy current conductivity standard be very close to the vacuum value. Only Cu-based alloys are potentially capable of meeting this criterion in the needed conductivity ranges. Special melts are indicated because current industrial practice is to add significant quantities of Fe, Co, and Mn (which can develop full magnetic moments or form magnetic precipitates in Cu) as grain refiners or to improve mechanical properties. Currently available Si-bronzes contain 0.8 w/o Fe; Cupro-nickels, 1.0 w/o Fe; brasses, 0.05 percent Fe. Yet the brasses, for example, must contain less than 0.03 percent Fe if Fe precipitation is to be avoided during stress relief.

In view of the importance of the magnetic properties, we have assembled and tested equipment for the measurement of magnetic susceptibility by the Gouy method. We are currently working on two sets of 100 coupons each of oxygen frequency high conductivity (OFHC) Cu and Ti-6-4 alloy.

#### Acoustic Emission for NDE Surveillance and Quality Control Subtask 12 of Task 12142

J. A. Simmons, R. B. Clough, H. N. G. Wadley, and R. Mehrabian

Acoustic emission refers to a technique for the measurement of elastic stress waves emitted by rapid dynamic changes of state in materials. AE can be used to detect, monitor, and measure the occurrence of plasticity, cracking, phase transitions, and corrosion where they are accompanied by rapid stress changes. Consequently, AE has unique potential as a passive surveillance tool for the control of microstructure during materials processing, monitoring fabrication of components and detecting, locating and characterizing flaw growth in structures. It also promises to provide a new tool for the quantitative measurement of the dynamics of material changes of state.

The structure of the stress waves emitted during acoustic emission is complex, and until recently the general formulism establishing the relationships between stress change sources and the amplitude and temporal character of the emission they provide was only poorly understood. Recent work at NBS has addressed these problems. This work demonstrated:

- Existing measurement methodologies that have evolved to date make use of only a small fraction of the potential information contained in acoustic emission signals.

- The character of the emission will be controlled by synergistic interactions between metallurgical variables and the stress state.

In spite of these difficulties, the technique is increasingly successful in finding application for monitoring cracking and predicting failure in ceramics, composites, and metal weldments. However, it also has the potential to make a great contribution to the monitoring of metals processing where it could provide essential data for feedback control improving quality and productivity, but this has received scant study in the past.

At NBS, a unique approach to the measurement of acoustic emission is being developed which has as its objective reconstruction of the source dynamics. This technique, which is similar to that currently revolutionizing the field of seismology, utilizes simultaneous high speed measurements (at different locations) of the initial wavefronts from individual emissions to allow quantitative reconstruction of the source stress drop. At least six observation channels are necessary for reconstruction of the six stress drop components as a function of time. To implement this advance in AE measurement methods:

- A computer based multichannel AE system has been constructed.
- New experimental methods for controlled generation of AE sources developed.
- New theoretical techniques of forward modeling and inverse filtering devised for signal analysis.
- Publication for deconvolution theory for multichannel experiments.
- Critical experiments will be carried for verification of multichannel AE analysis using a Nd:YAG laser and plate geometry.
- Correlation of AE signals, microstructural analysis and thermodynamic parameters of rapidly solidified electron beam source in aluminum and an aluminum alloy.
- A set of critical experiments designed to establish the validity of these new measurement methods.

Parallel studies drawing upon the above techniques, have examined flaw growth as part of the joint NBS/EPRI program in AE and explored the use of AE for monitoring rapid solidification as part of the DARPA/NBS project in Rapid Solidification and NDE.

Our program during the past year can be broken down into four categories:

- (1) Theoretical advances.
- (2) Experimental verification of source characterization.
- (3) Experimental method for the controlled generation of AE in A533B pressure vessel steel.
- (4) AE studies of rapid solidification.



## (1) Theoretical Advances

The theoretical framework for acoustic emission sources rests upon Green's function formalism for stress waves generated by changes in internal stress induced when a source responds inelastically to structural loads. The forward formulation, in which the emission from a source of known character is deduced, has been published in Theory of Acoustic Emission, Proceedings of the International Conference on Dislocation Modeling of Physical Systems, Pergamon Press, 1981.

There the representation of an AE source event was first given in multipolar expansion form and then restricted by two assumptions, the pseudopoint approximation and the Stump-Johnson representation, to avoid the technological difficulties associated with high moment components. The key restriction for validating these assumptions is a band limiting process to restrict the frequencies to a region called The Informative Band. Estimates of the limiting frequency for the band were given as a function of defect size and shape. Within the informative bandwidth one can develop a transfer function formalism which allows one to consider transmission of the information frequency by frequency from the source through the structure to the detector: outside this band specific models of the details of the AE mechanism are required to deduce AE signals.

The general formulation of acoustic emission from plasticity, cracks, and phase transformations was then developed within the pseudopoint approximation using the concept of retarded dipole density to deal with the problem of time delays from emission from propagating cracks and phase change regions. The radiation patterns for defect sources are highly directional and depend on source type and orientation (see figs. 11 through 13). Finally, the concepts of stress controlled and materials controlled acoustic emission were introduced and the synergistic relation between the ambient stress field and microstructural constraints were discussed.

Subsequent work has concentrated on the inverse problem for deducing the character of the stress drop components from measured acoustic emission signals. This is one of a class of "remote sensing" problems in which small amounts of measurement error or noise can obscure the information about the source signal. Sophisticated signal processing techniques are demanded.

The transfer function formalism leads to simultaneous convolution equations describing the acoustic emission signals in terms of the source stress drop components, the structure response, and the transducer characteristics. These simultaneous equations can be reduced to a single deconvolution equation which is, in general, even more ill-conditioned than deconvolution problems encountered in time series applications.

A singular valued decomposition (SVD) algorithm developed in conjunction with D. O'Leary (Division 711), A Bidiagonalization-Regulatization Procedure for Large Scale Discretizations of Ill-Posed Problems, SIAM Journal of Statistics and Computing, December 1981, has been applied to



such signals. Since the full SVD algorithm is prohibitively demanding of computer resources for problems of the type required in acoustic emission, the above procedure uses a reduced dimension representation similar to the Rayleigh-Ritz procedure. The SVD algorithm both inverts and filters to produce a number of candidate solutions to the inverse problem. The results obtained, while promising, suffer from the difficulty that it is difficult to select the "best" approximation from among the candidate solutions.

To help deal with this problem and to examine the possibility for new pattern recognition techniques for source signatures, an alternate approach is being studied. This approach uses a modification of the Z transform of the time series to be inverted which allows powerful complex variable techniques to be combined with linear algebraic methods for inverse filtering. In this approach the Z transform of the time series becomes a polynomial of high degree (typically 512 or higher). An entirely new set of algorithms has been developed which finds all the zeroes of such high degree polynomials and uses these for both pattern recognition purposes and to develop new noise filters which are supplemental to those obtained in the SVD approach and can be used to greatly reduce solution noise while allowing a priori information about the frequency content of the solution to be factored in.

These new algorithms, which must be applied to time series of great length to be usable in acoustic emission inversion, are currently being employed to find robust procedures for deconvolution. An example of the types of candidate solutions obtained in carrying out deconvolution (in this case of a 43-point time series based on the surface-to-surface Green's function for a half-space) is illustrated in figures 14 through 20.

## (2) Experimental Verification of Source Characterization

The objective of source characterization is measurement of the magnitude, orientation and time dependence of the stress drop tensor of acoustic emission sources. The stress tensor provides the basic information required for defects assessment in NDE and, in the laboratory, promises to provide dynamic information that would greatly advance our understanding of the dynamics of metal deformation and phase transformation processes. A formalism based upon dynamic elasticity has been developed which, in principle, provides us with a framework for deducing the stress drop tensor. Instrumentation to implement this approach has also been compiled. Now, a critical series of experiments are underway in which the stress drop tensor is to be measured using acoustic emission techniques and compared with that independently deduced by measurement or predicted from well developed theory.

The problem is that there are no available techniques for the measurement of stress drops when they occur at velocities close to that of the speed of sound. One possible approach we are following is to use reproducible cracking under indentation loading and this is discussed below. However, another possible approach is the use of a simulated reproducible acoustic emission.

The ideal simulated source should be composed of dipole forces of similar magnitude and orientation to those of natural AE and have a time duration between 10 ns and 10  $\mu$ s (the range of the majority of natural emissions). These properties should be predictable and/or independently measurable. We have set up a laser generated thermoelastic simulated acoustic emission source for critically evaluating the performance of multichannel source characterization.

The thermoelastic dilatational strain accompanying absorption of pulsed laser radiation has been modeled as a combination of force dipoles whose strengths were calculated using thermal diffusion theory. The temporal behavior of the elastic displacements due to each dipole component were then evaluated from the dynamic elastic Green's tensor for an isotropic infinite plate. The displacement waveform for the complete source was then obtained by linear superposition of the individual dipole responses.

The thermoelastic source generates longitudinal, transverse, and surface waves. When calculations of displacement are performed on the same surface as the source, the waveforms are dominated by surface waves, particularly at large source-receiver distances. When calculations are made on the surface of the plate opposite the source, the transient displacement waveforms are dominated by head-waves. These latter waves have a nonunique ray speed and would lead to ambiguous source locations in acoustic emission monitoring.

Wide bandwidth response instrumentation system has been designed and constructed that can measure displacement down to a sensitivity of  $\sim 10^{-14}$ m over a 2.5 MHz bandwidth. This has been used to measure the displacement waveforms from the thermoelastic expansion accompanying the absorption of Nd:YAG laser pulses of 25 ns duration.

The measured waveforms contain the features predicted by theory and the dipole magnitudes are, within experimental error, in agreement with these predicted. From this encouraging basis we are proceeding to apply the deconvolution procedures developed above to deduce the full tensor description of the source stress change.

### (3) Experimental Method for the Controlled Generation of AE in A533B Pressure Vessel Steel

Here the objective, for the nuclear power industry, has been the development of an experimental technique for localized production of reproducible AE signals (by indentation) in A533B pressure vessel steel and the correlation of these signals with the defects and microstructure at that location.

These steels, while in the normalized condition are nonemissive, can become embrittled and emissive during fabrication into nuclear reactor pressure vessels by improper welding and heat treating practices (temper embrittlement), and can be further embrittled during service due to hydrogen, which is a fission product. Recently the NRC announced (Newsweek, April 19, 1982) that 8 of these vessels in service are becoming embrittled at a much faster rate than the originally expected 40 year



lifetime--down to a few years. It would seem that the above effects could contribute synergistically with the normally present radiation embrittlement and stress corrosion to reduce those lifetimes.

By controlling the tempering and hydrogen charging in A533B we succeeded in producing AE from virtually none in the normalized condition up to an activity as high as that of borosilicate glass in the fully embrittled condition. We were further able to relate the sources of emission as being due to microcrack nucleation ( $\sim 5$  micron) at MnS inclusions (fig. 21) in the temper embrittled state and growth to larger grain boundary cracks ( $\sim 250$  micron) with the addition of hydrogen. A very significant result was the unexpectedly prominent role played by the MnS inclusions in the temper embrittlement process, as opposed to the usual attention given to segregated grain boundaries. This aspect is being followed up by work at Harwell.

#### (4) AE Studies of Rapid Solidification

Rapid solidification is a new technique used for producing metallic glasses, which provide low loss transformer core material, and it is also used to produce superior surface coatings and long wearing bearing surfaces. AE can be used to monitor rapid solidification surface modification to detect flaws produced during processing. It also promises to provide dynamic information on the solidification process itself since a typical solidification time for a surface melt is on the order of 100 ms and stress waves can be monitored over considerably shorter times ( $\sim 100$   $\mu$ s). Very little work has been done in this area and due to the potential of AE to shed light on this subject, NBS and DARPA are sponsoring research on AE monitoring of rapid solidification processing.

Because of its commercial applications in welding and surface modification, the electron beam was used as a directed energy source for melting. A new technique has been developed for studying solidification of such melts. First it was verified that the signals were not electrical noise and were caused by material changes during solidification. The experimental approach consists in irradiating a spot on a plate, producing a steady-state melt at  $2 \times 10^5$   $\text{Wm}^{-1}$  for flux density/radius (qa) (the product of the heat flux density and the source radius), switching off the electron beam to eliminate it as an AE source, then monitoring the amount of energy produced by AE during solidification.

Our first results show the effects of alloying on resolidification AE. The resolidified melts in the 2219 aluminum alloy contained numerous cracks which indicate that hot tearing during solidification is the cause of the AE in the 2219 alloy (fig. 22). In contrast, the 1100 aluminum resolidified melts had virtually no cracks (fig. 23). This is reflected also in the amount of energy emitted acoustically during resolidification for the two materials (figs. 24 and 25).

Results of this type are of great interest to the rapid solidification field and these represent just the preliminary results. Once the sources of AE in rapid solidification are more fully ascertained, steps can be made to implement AE monitoring of surface modification processes. In



addition, once the sources of AE are ascertained, it is expected that these can be used for dynamically observing the solidification process and the kinetics involved.

#### Magnetic Particle Inspection Standards

##### Subtask 13 of Task 12142

L. Swartzendruber

This project was initiated by the Specification and Technical Data Branch of the Army Materials and Mechanics Research Center, Watertown, MA. Military Specification MIL-M-11472, Magnetic-Particle Inspection; Process for Ferromagnetic Materials, is being reviewed for proposed revision or cancellation and replacement by Military Specification MIL-STD-271, Military Specification MIL-I-686, or American Society for Testing and Materials Recommended Practice E709-80. The contents of these documents have been compared with current state-of-the-art practice in magnetic particle inspection as revealed by industrial practice, available literature, current applicable Military Standards, Aerospace Materials Specifications, and American Society for Testing and Materials documents. A draft version of a revised MIL-M-11472 has been prepared. Feedback from Department of Defense users will be used to eliminate or review portions as deemed necessary.

#### Magnetic Measurements

##### Subtask 14 of Task 12142

L. Swartzendruber

Nondestructive evaluation methods utilizing "magnetic leakage fields" are widely used for detecting defects in ferromagnetic materials such as iron and steel. These methods involve the magnetization of the material and the subsequent detection of the leakage fields resulting from any defects which might be present. A common technique for detection of leakage fields is magnetic particle inspection (MPI). MPI involves the spraying or flowing of minute magnetic particles over the magnetized material. Patterns are formed on the surface which indicate the location of surface or subsurface defects. This method reveals the presence and location of defects, but gives limited information about their size, shape, or depth below the surface. Other methods, such as measurement with a Hall probe or moving coil, give more quantitative information about the leakage field, but correlation of the measured field with the shape and location of the defect also presents considerable difficulty.

In a material of constant permeability, analytical calculations for various geometries, such as a long transverse cylinder, are possible. We have previously shown that measured magnetic leakage fields above artificial cylindrical defects in a steel sample are considerably larger than the strength calculated analytically for a material of constant permeability, however high that permeability might be. Clearly, the nonlinear B-H relationship has a significant effect in this type of measurement. Thus, any mathematical model of such a system which incorporates permeability as a constant is insufficient; permeability must be

incorporated into the model as a function of the field strength. This complication necessitates numerical solutions which require lengthy calculations for each specific case.

Utilizing a nonlinear finite difference method, and an analytical representation of the nonlinear B-H relationship, numerical calculations have been performed on the Metallurgy Division computer. The numerical method was used to calculate leakage fields for subsurface defects and for slits open to the surface. For comparison, linear calculations were also performed. These calculations were then compared with experimental measurements. The nonlinear numerical calculations are in qualitative agreement with the experimental measurements and confirm that: (1) the leakage field perturbation due to the defect continues to increase well into the saturation region of the magnetization curve; (2) the leakage fields have a shape nearly that expected from a linear magnetic dipole; and (3) nonlinearity causes the defect to appear closer to the surface than its actual physical distance and stronger than predicted by a linear theory.

A critical factor in obtaining successful MPI results is the choice of a proper magnetizing level. Often it is assumed that, for the MPI technique, the applied field strength at the point of maximum permeability should be used as the field strength in order to yield optimum test results. However, the correlation we have obtained, both experimentally and theoretically, demonstrates that this is not a correct assumption. Other factors, and not the maximum sample permeability, place an upper limit on the applied field strength for optimum results.

Our results show that the magnetic leakage field continues to grow nearly in proportion to the applied field out to very large applied fields. The optimum applied field for MPI is thus the largest allowable subject to other constraints. These constraints involve mainly the effect of stray fields, i.e., fields which arise from end effects, surface finish, etc. These stray fields have a number of deleterious effects. They can, for example, cause the particles to be swept past the defect at too high a velocity to be "captured" by the leakage field, or they can cause particles to be attracted to the surface over large areas, contributing to a background which can mask indications from real defects.

Thus, we find that the value of the applied field in the vicinity of the defect is more important than the magnetization level of the material. This applied field can be effectively determined using a small Hall probe, or other suitable field measuring device, located so as to measure the component of magnetic field parallel to the sample surface and as close to the sample surface as possible. This has important consequences for obtaining reliable and reproducible magnetic particle inspection results, especially on parts which are not of simple geometric shapes. The effectiveness of various methods of magnetization, current levels, etc., can be readily assessed by easily made Hall probe measurements.



Development and Application of a Second Generation Image Intensifier for  
Real Time Microradiography  
Subtask 15 of Task 12142

M. Kuriyama, W. J. Boettinger, H. E. Burdette, and R. D. Spal

The resolution of real-time radiographic systems is often dictated by the spatial resolution of viewing detectors. To overcome this difficulty, an x-ray image magnification technique was developed [12,13]. This development does not, however, negate any further improvement of the spatial resolution of image detectors. As a continuing effort seeking a better detector, we have employed a double intensified charge injection device (ICID) camera to develop an x-ray image intensifier. This ICID camera is, in effect, a modified solid-state charge-couple TV camera.

In general, there are two approaches to obtain optical signals from x-ray photons: (a) direct photon-electron conversion in videcons; and (b) visible photons converted from x-ray photons by a phosphor, and subsequently viewed by an optical image intensifier. In this work, we chose the second approach. Phosphors of different particle sizes were prepared on fiber optics plates ( $\sim 30 \mu\text{m}$ ). The ICID camera was tested by a wedge-shaped resolution test pattern after one of the fiber optics plates was mounted tightly in front of the camera. Typical results are 2.9 line pairs/mm for FG3M phosphor and 4.5 lp/mm for P20 phosphor ( $4.3 \text{ mg/cm}^2$ ) by visual test. The last value corresponds to limiting resolution  $110 \mu\text{m}$ .

To determine quantitatively the degree of resolution in this system and determine quantum efficiency, another set of measurements was made using this system with the two kinds of phosphors. The ICID camera was operated in photon counting mode, that is, low flux, high gain mode. The image output was digitally processed, using a video frame grabber and a digitizer interfacing LSI 11/23. With the P20 phosphor, the order of 4 pixels in radius per a single photon was observed. One pixel is  $40 \mu\text{m} \times 30 \mu\text{m}$ . This result agrees with the visual result of  $110 \mu\text{m}$  limiting resolution (5% MTF).

Quantum efficiency was found to be 100 percent with a thick phosphor. The thinner phosphor, the higher the resolution, but less quantum efficiency, as predicted. The decay time of the phosphors was much shorter than the TV frame period ( $\sim 30 \text{ ms}$ ).

This system was used to obtain video tape images from dental teeth, indentation impressions on a NaCl crystal and a copper crystal in the microradiography mode. This system was also used to record real-time data from various crystals in the x-ray diffraction topographic mode using synchrotron radiation.

[12] Boettinger, W. J.; Burdette, H. E.; Kuriyama, M. Rev. Sci. Instr. 50: 26; 1979.

[13] 1978 NDE Annual Report.



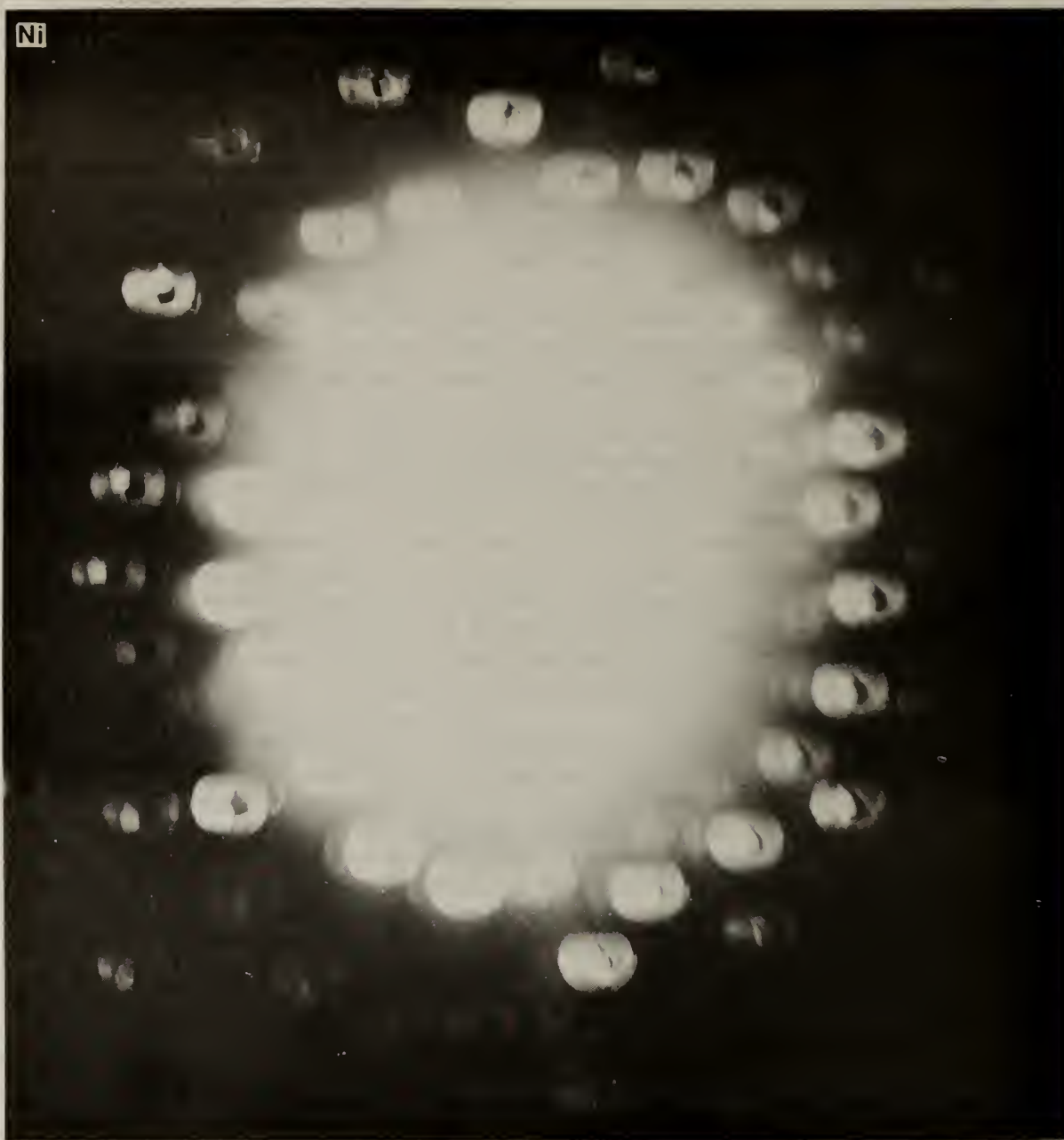


Figure 1 Synchrotron white beam transmission topograph of Czochralski grown Ni crystal containing subgrains. Note the changing shifted position of the oval shaped subgrain in various Laue spots around the central spot.



Figure 2 Synchrotron white beam transmission topographs of an electron beam melted and resolidified spot on a 111 surface of Si. Notice the residual stress pattern which extends outward from the weld spot.



Figure 3 Synchrotron white beam topographs of single Al powder particles solidified with large undercooling. The top left shows a particle which is a single crystal and which had only one nucleus. The top right shows a particle having two grains while the bottom left shows a deformed particle.



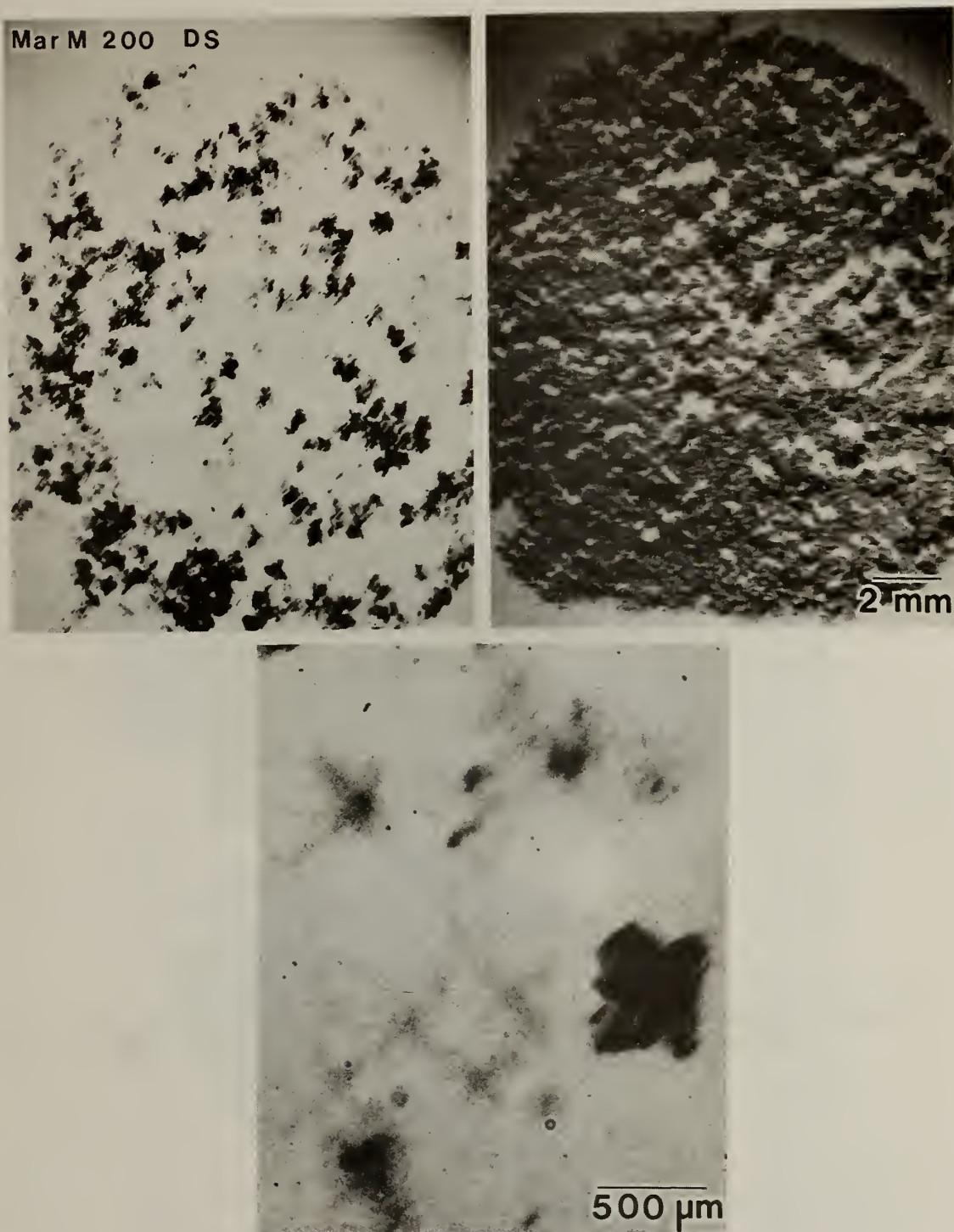


Figure 4 ACT topographs taken of a directionally solidified  $[(001)]$  Mar M 200 monocrystal. The mosaic structure is evident in the top left and full diffraction is obtained by rocking the crystal  $1^\circ$  during exposure. The bottom picture is an enlargement showing a grain composed of a single dendrite.



Figure 5 Enlarged view of 040 white beam topograph of Fe-24 at. % Al grain showing dumbbell image contrast of inclusions.

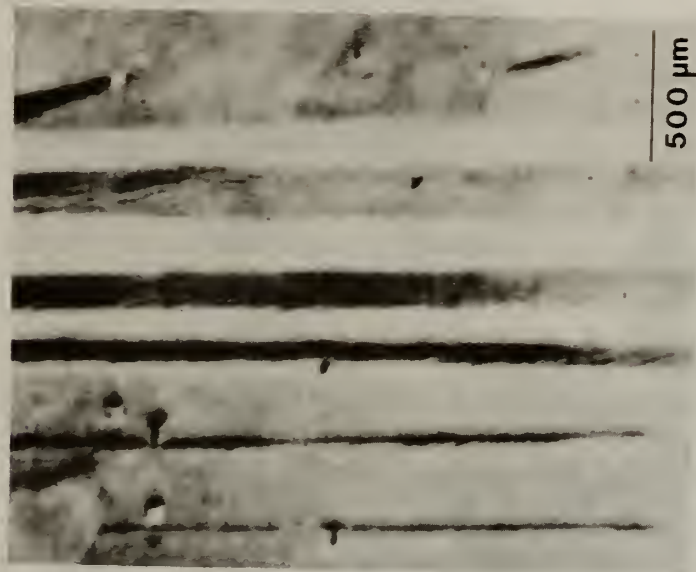


Figure 6 ACT surface reflection topographs of grain in Fe-24 at. % Al alloy. Note the subgrains within the large grain as well as the magnetic domain images.

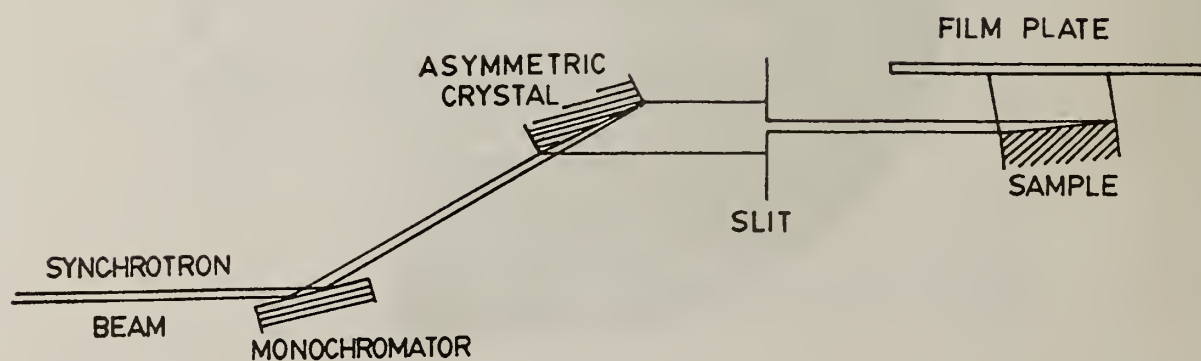




$\bar{1}00$   
010

$\leftarrow \bar{H}(0\bar{4}4)_{NP}$

.3 mm



## SYNCHROTRON RADIATION TOPOGRAPHY OF SODIUM CHLORIDE

8 KeV Synchrotron Radiation Operated at 5.25 GeV 16 mA  
Exposure Time : 5 minutes on Ilford L-4 50 $\mu$ m Nuclear Emulsion Plate

Figure 7 An  $0\bar{4}4$  topograph of an indented NaCl crystal taken at the exact Bragg angle. The inset illustrates an x-ray optical arrangement for changing the glancing angle  $\theta_{in}$ .

# SYNCHROTRON RADIATION TOPOGRAPHY OF COPPER CRYSTAL IN THE BRAGG GEOMETRY

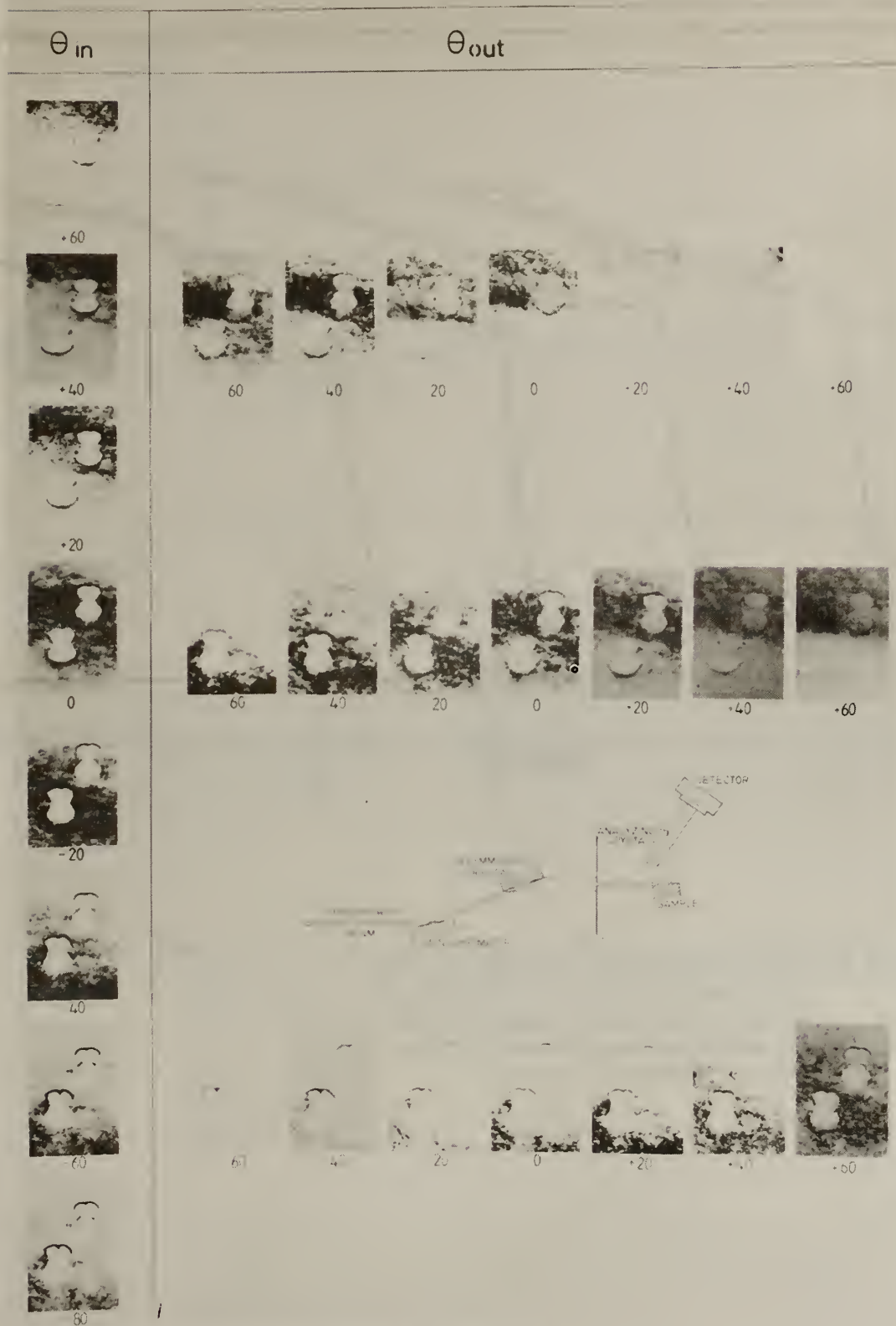


Figure 8 A series of topographs from a Cu crystal with Knoop indentations. Each topograph was taken at a different glancing angle  $\theta_{in}$  and a different observation angle,  $\theta_{out}$ . This set of topographs opens up a new avenue for quantitative characterization.

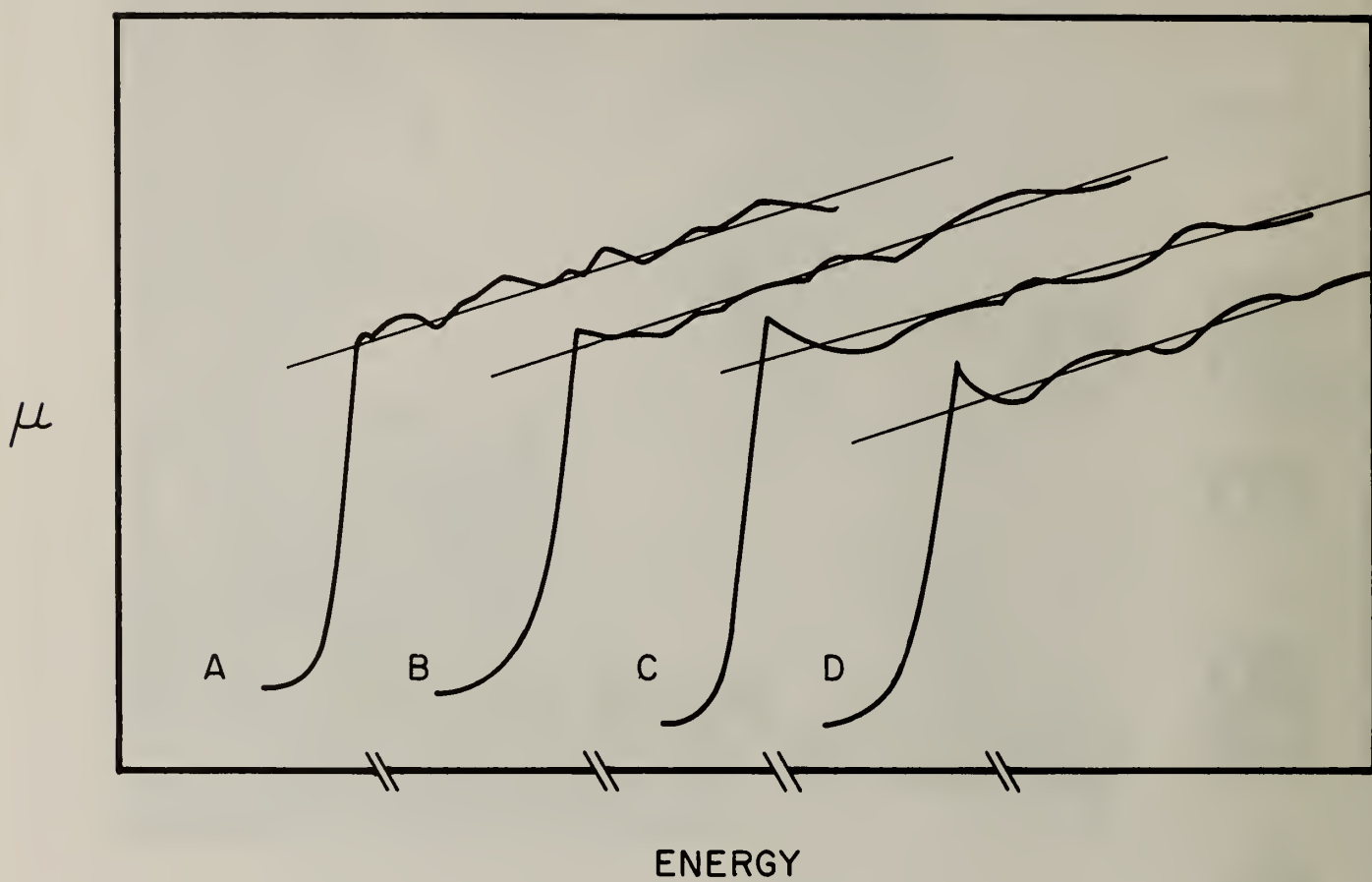


Figure 9 Near-edge absorption spectra for  
(a) pure Fe  
(b) chromate-passivated Fe film  
(c) nitrite-passivated Fe film  
(d) air formed film on Fe



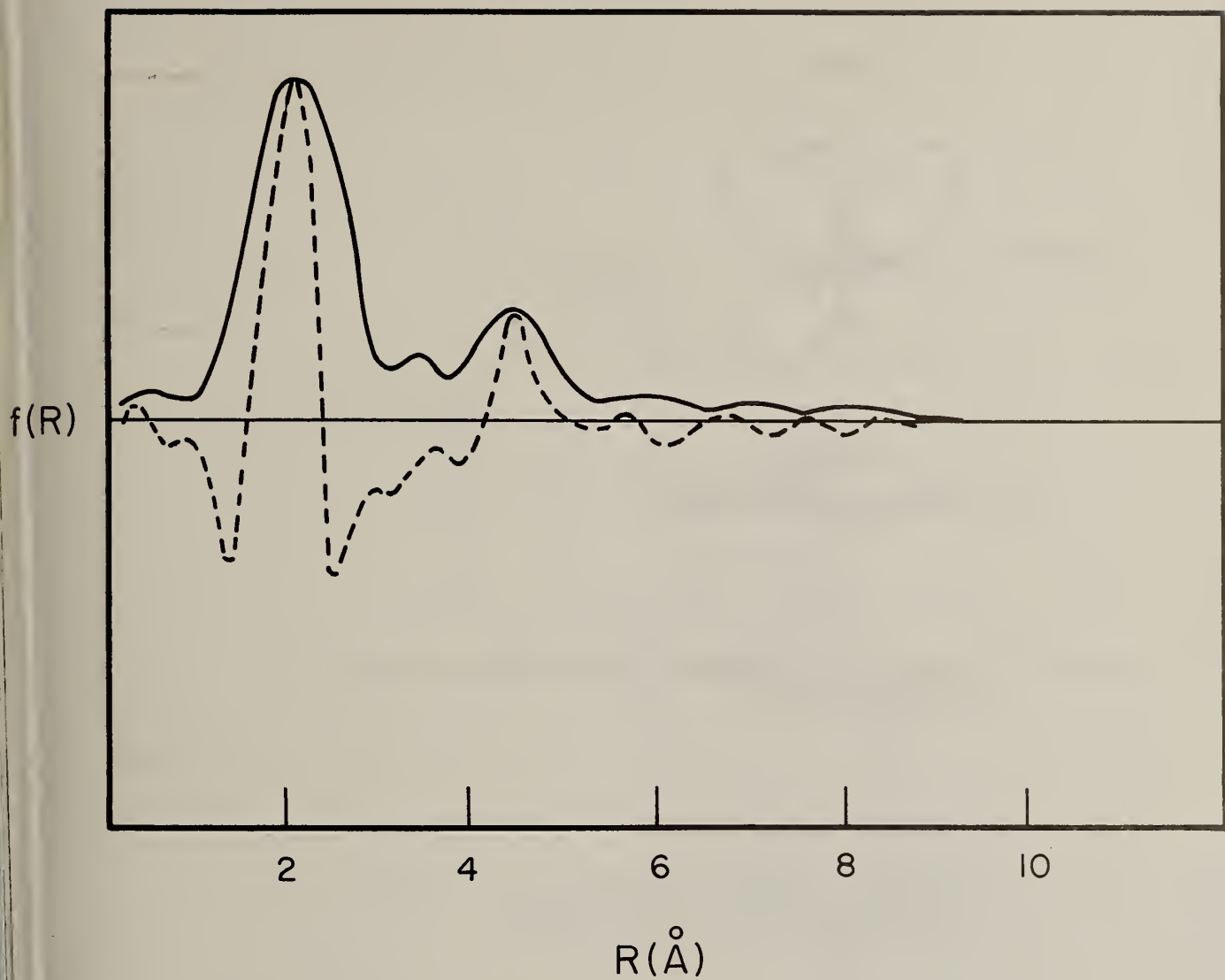


Figure 10 Fourier transform of the spectrum shown in figure 9(b).  
Solid line shows the magnitude and the dashed line shows  
the imaginary part of the transform.

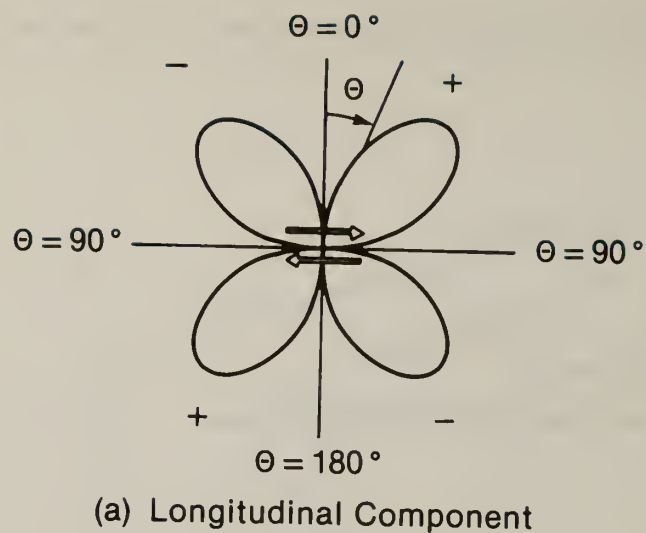


Figure 11 Longitudinal component radiation pattern for a dislocation source.

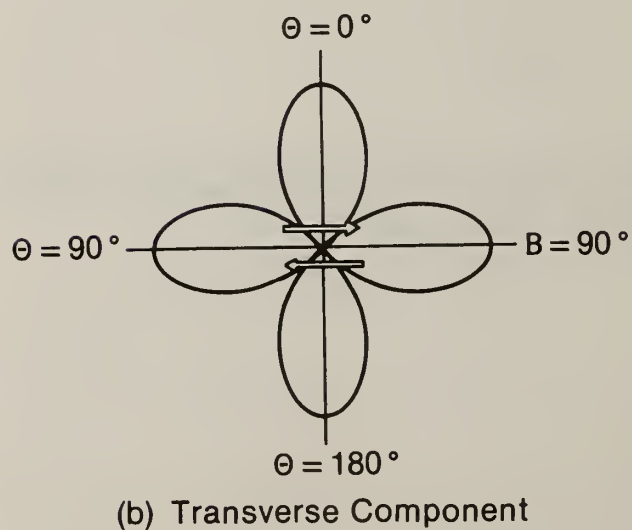


Figure 12 Transverse component radiation pattern for a dislocation source.

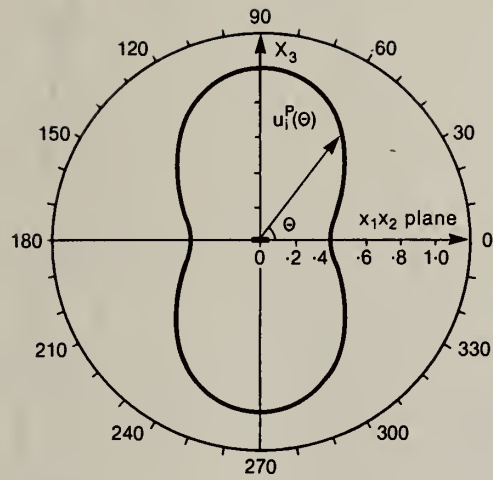


Figure 13 Longitudinal component radiation pattern for a microcrack source.



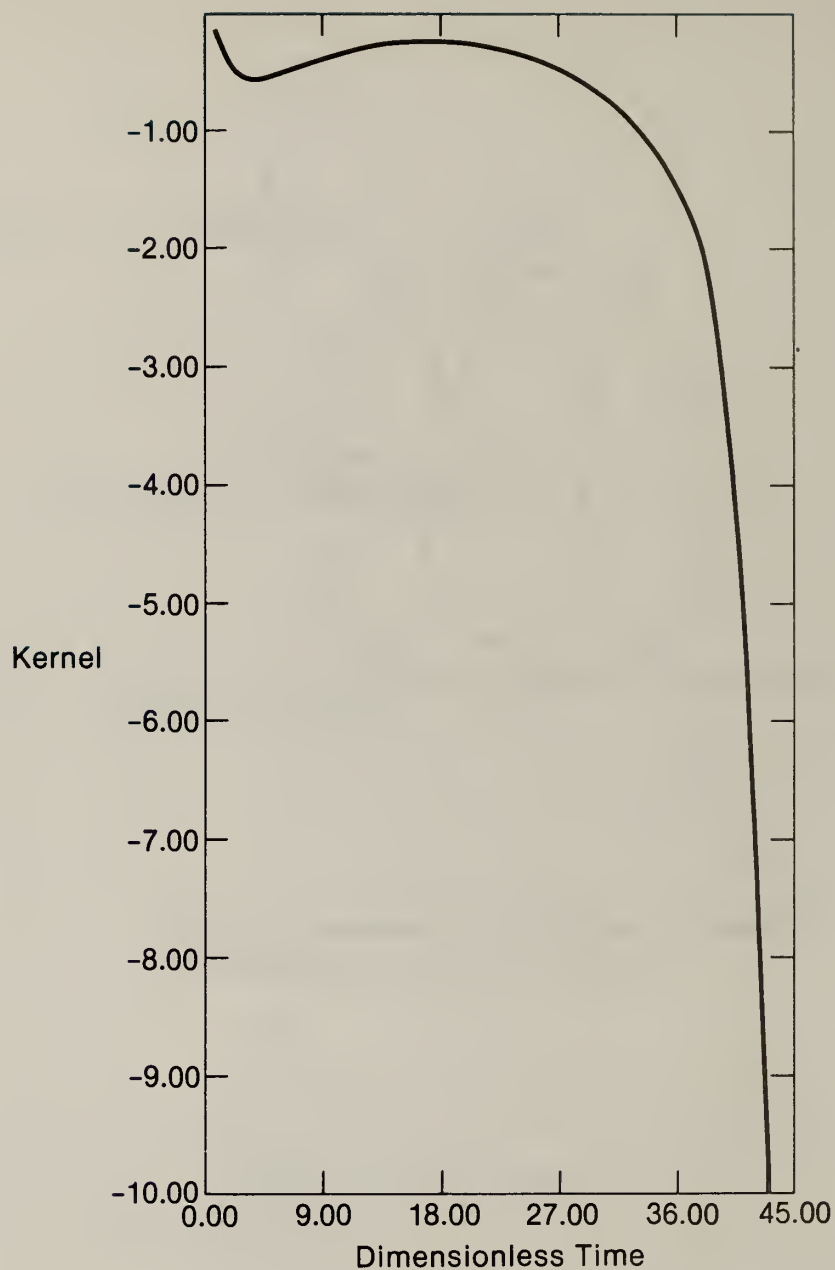


Figure 14 The beginning of the vertical response to a vertical force in a half-space with horizontal planar surface. This time series can be thought of as the kernel to be deconvolved out. This particular kernel is very ill-conditioned rendering deconvolution particularly difficult.

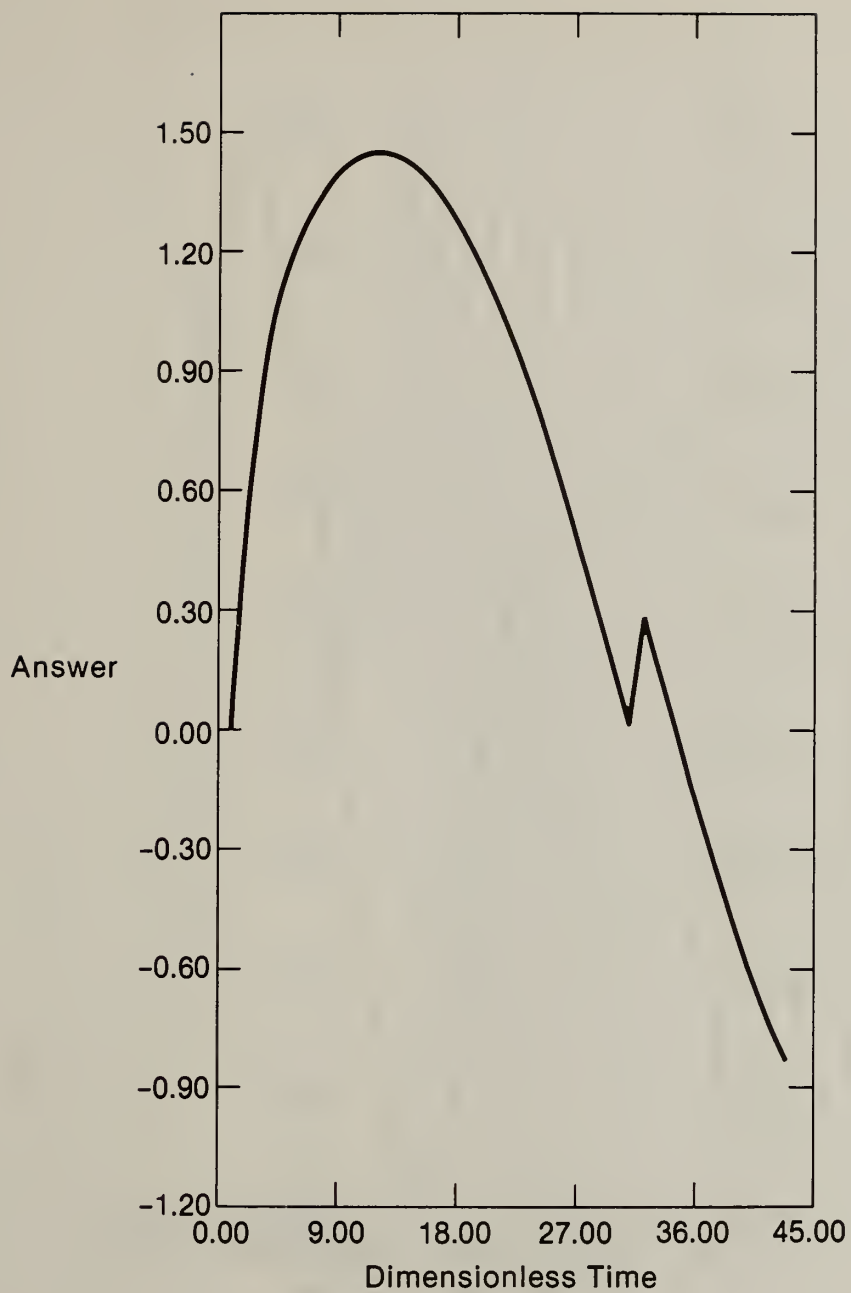


Figure 15 A hypothetical source curve. The 'answer' to be found.

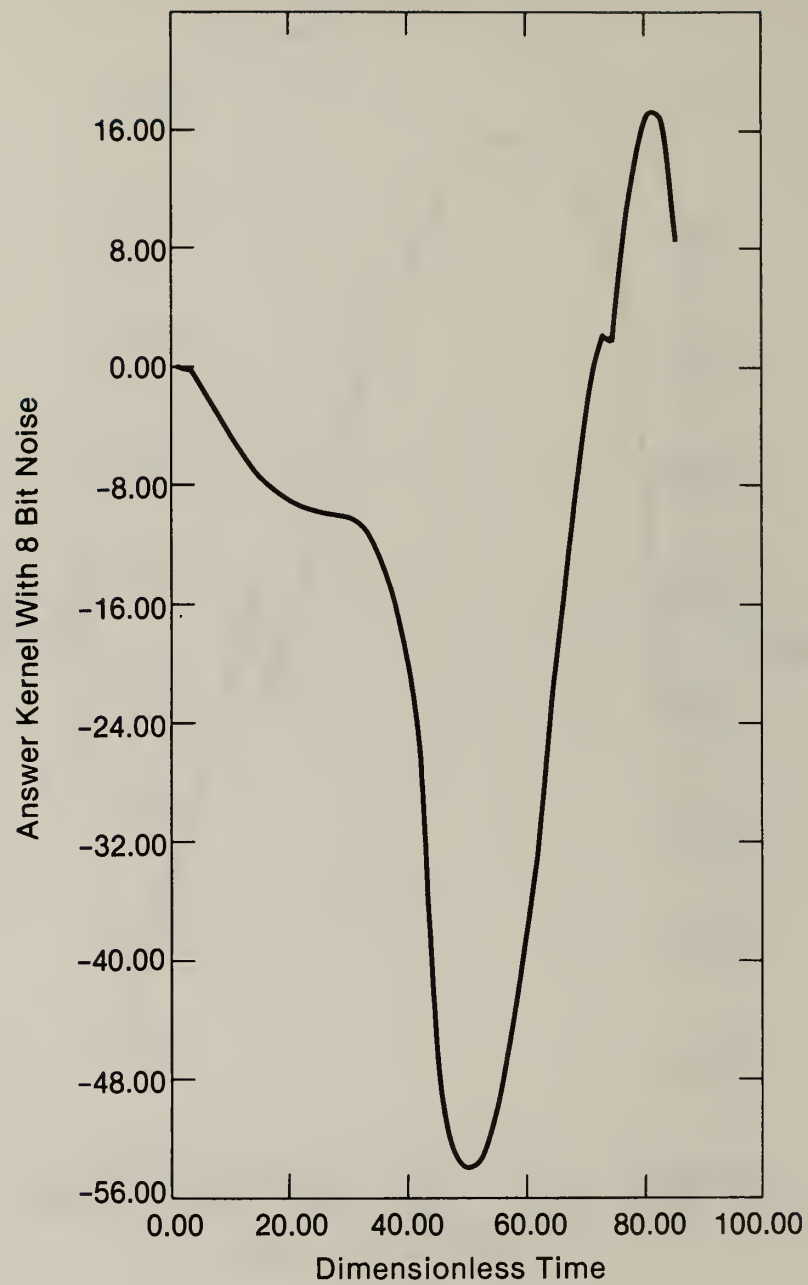


Figure 16 A hypothetical resulting output signal obtained from the convolution of the first two curves with 8-bit noise ( $\pm 0.2\%$ ) added.



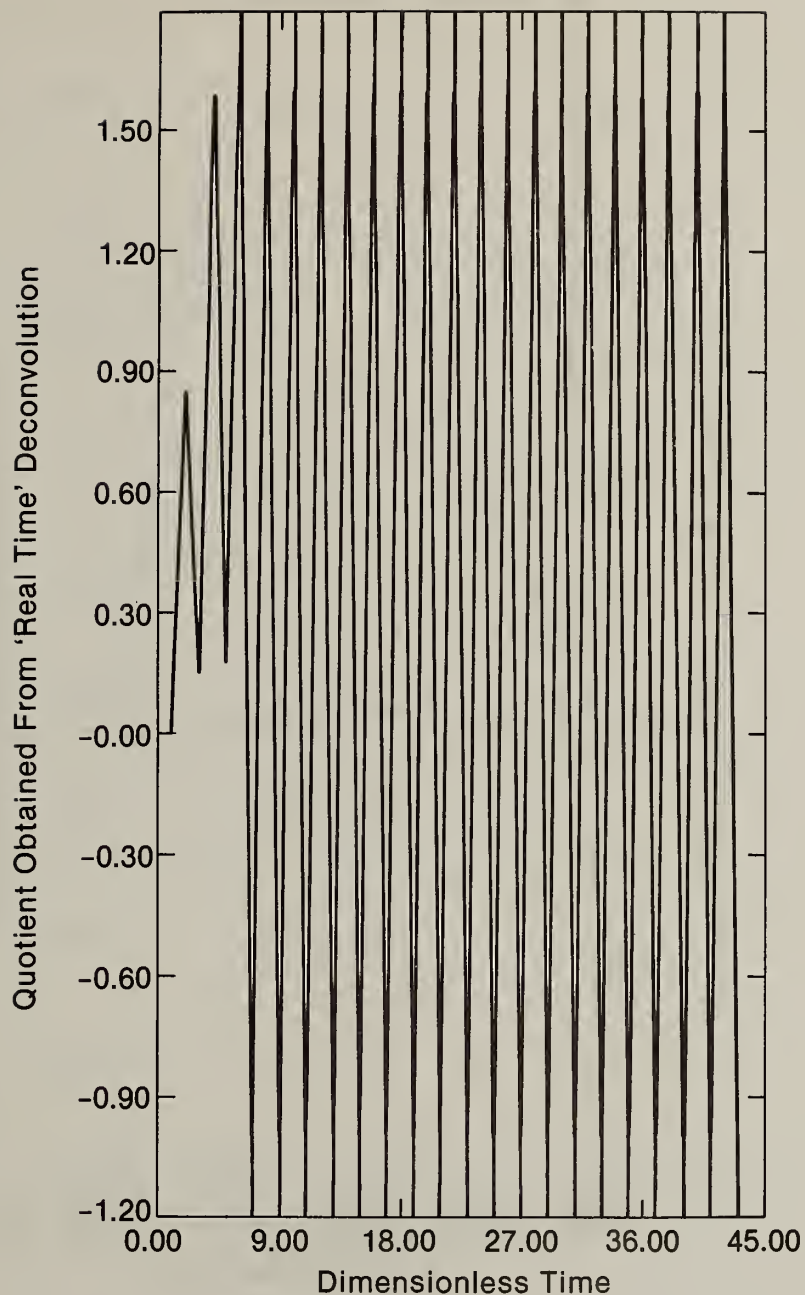


Figure 17 The approximation to the solution using 'real time' deconvolution which is simply the routine inversion of the convolution matrix as a lower diagonal matrix (compare with figure 5).  
 Note: This curve oscillates between  $\pm 10^5$ .

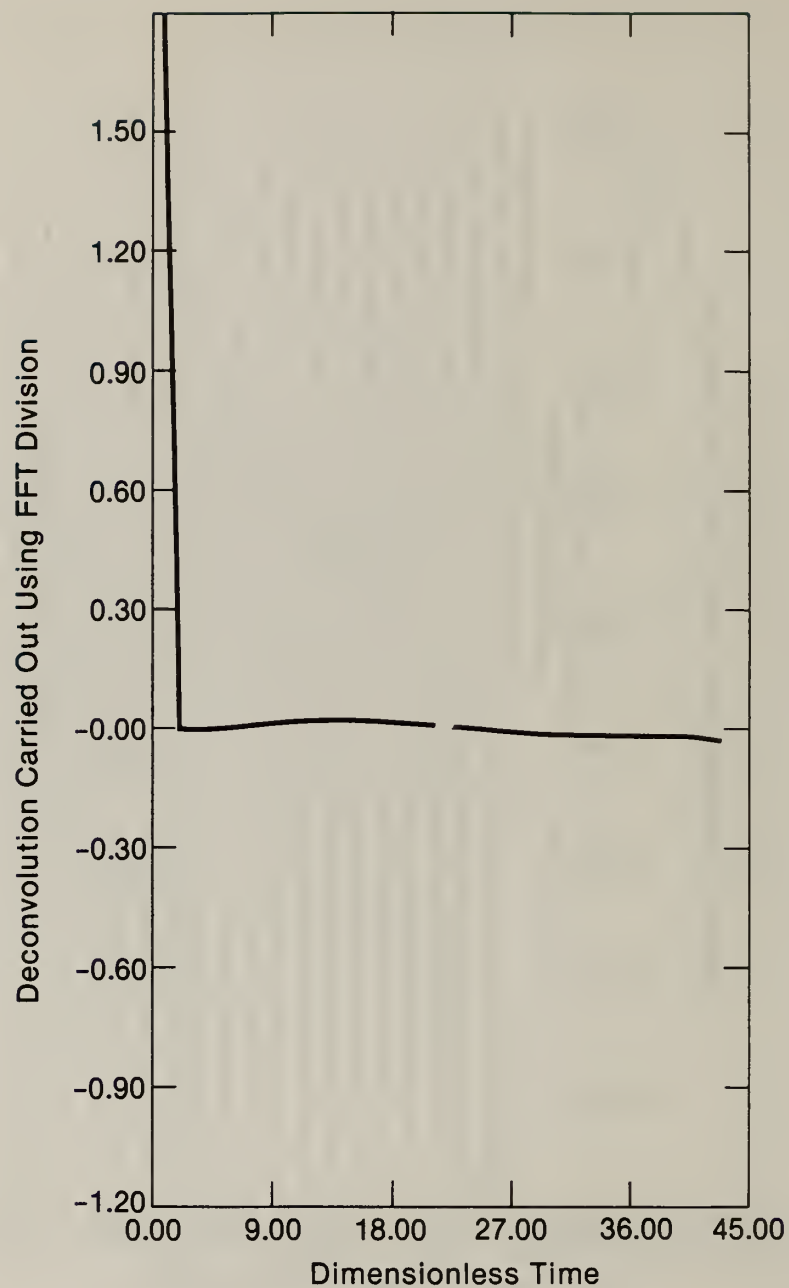


Figure 18 The approximation to the solution using division of the FFT of the output signal by the FFT of the kernel with 43-points of zero padding added to remove an obvious time aliasing error (compare with figure 5).

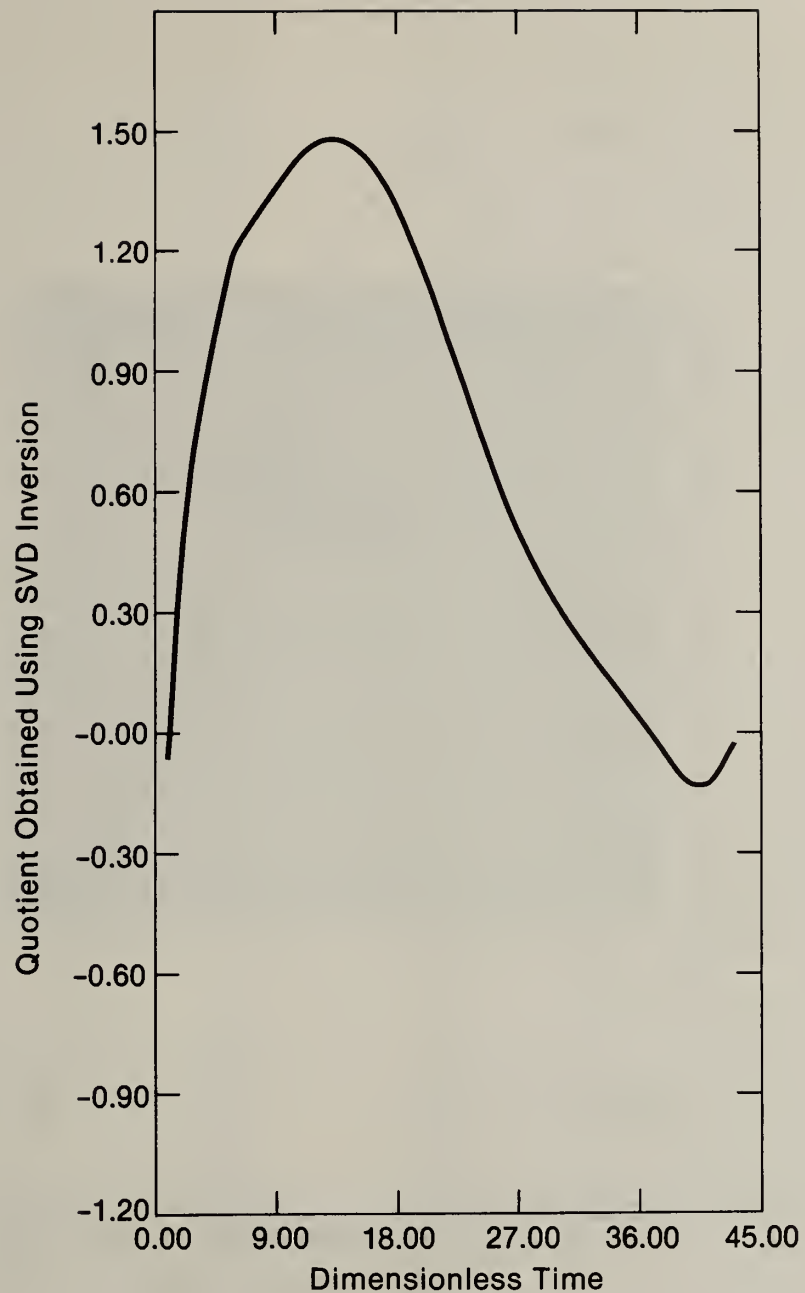


Figure 19 The 'best' approximation (in the sense of minimum error in the time domain) obtained from the SVD procedure (compare with figure 5). While obviously orders of magnitude better than the previous approximations, this approximation is in considerable error throughout the frequency domain.



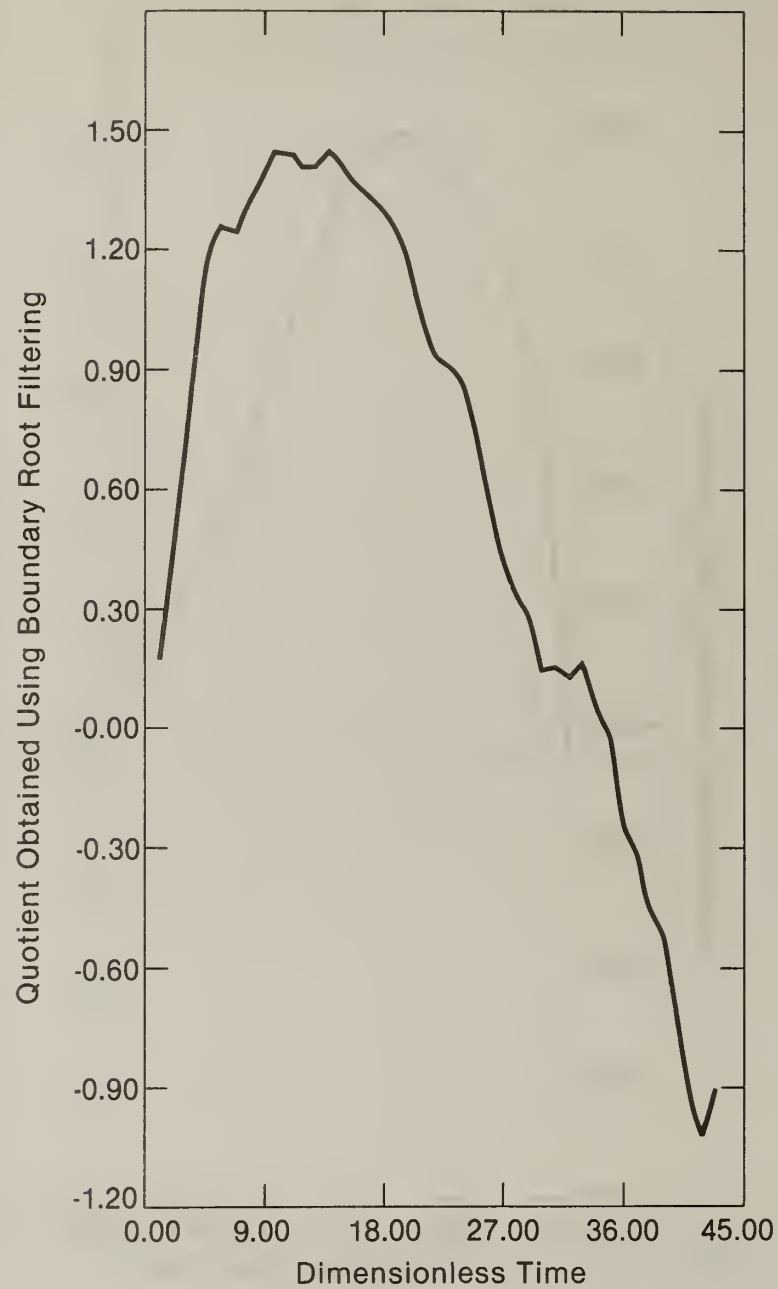


Figure 20 An approximation obtained using boundary-root filtering and radiused FFT deconvolution methods. This solution while appearing more 'jittery' than the preceding is actually more accurate in the frequency domain as well as giving a good approximation in the time domain (compare with figure 5).

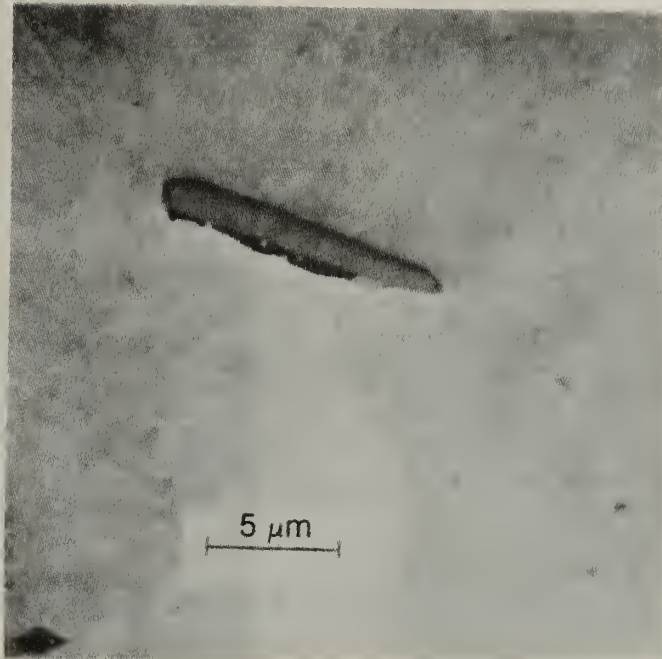


Figure 21 Debonding of MnS inclusion due to indentation of uncharged, temper embrittled A533B.



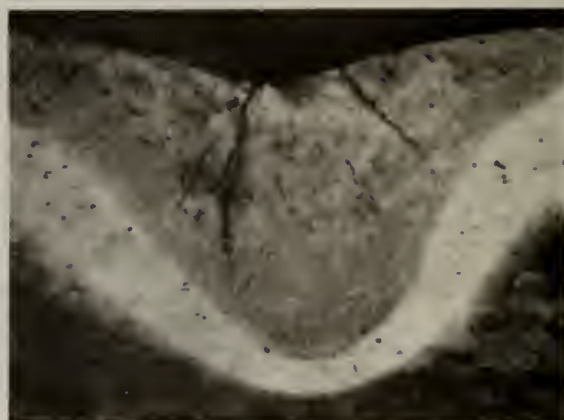
(a)  $1.9 \times 10^5 \text{ Wm}^{-1}$



(b)  $2.7 \times 10^5 \text{ ms}^{-1}$



(c)  $3.3 \times 10^5 \text{ Wm}^{-1}$



(d)  $4.1 \times 10^5 \text{ Wm}^{-1}$



(e)  $5.7 \times 10^5 \text{ Wm}^{-1}$



(f)  $6.4 \times 10^5 \text{ Wm}^{-1}$

0.5 mm

Figure 22 The effect of  $q_a$  upon melt profile and solidification microstructure of 2219 aluminum.





(a)  $1.9 \times 10^5 \text{ Wm}^{-1}$



(b)  $2.7 \times 10^5 \text{ ms}^{-1}$



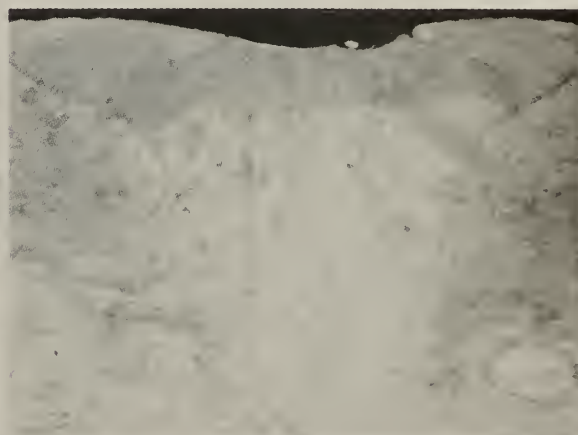
(c)  $3.3 \times 10^5 \text{ Wm}^{-1}$



(d)  $4.1 \times 10^5 \text{ Wm}^{-1}$



(e)  $5.7 \times 10^5 \text{ Wm}^{-1}$



(f)  $6.3 \times 10^5 \text{ Wm}^{-1}$

0.5 mm

Figure 23 The effect of  $q_a$  upon melt profile and solidification microstructure of 1100 aluminum.

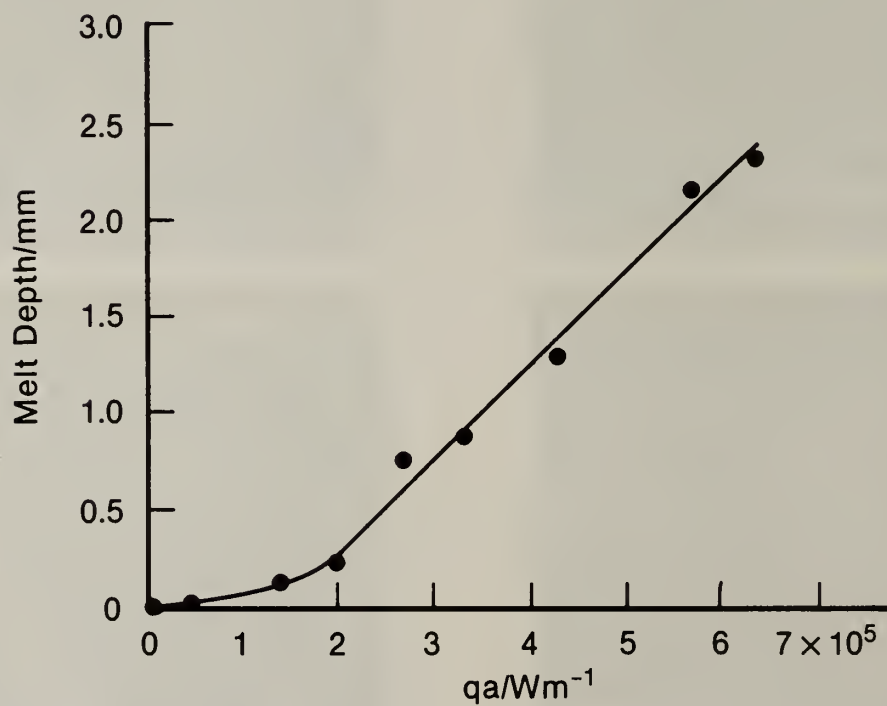
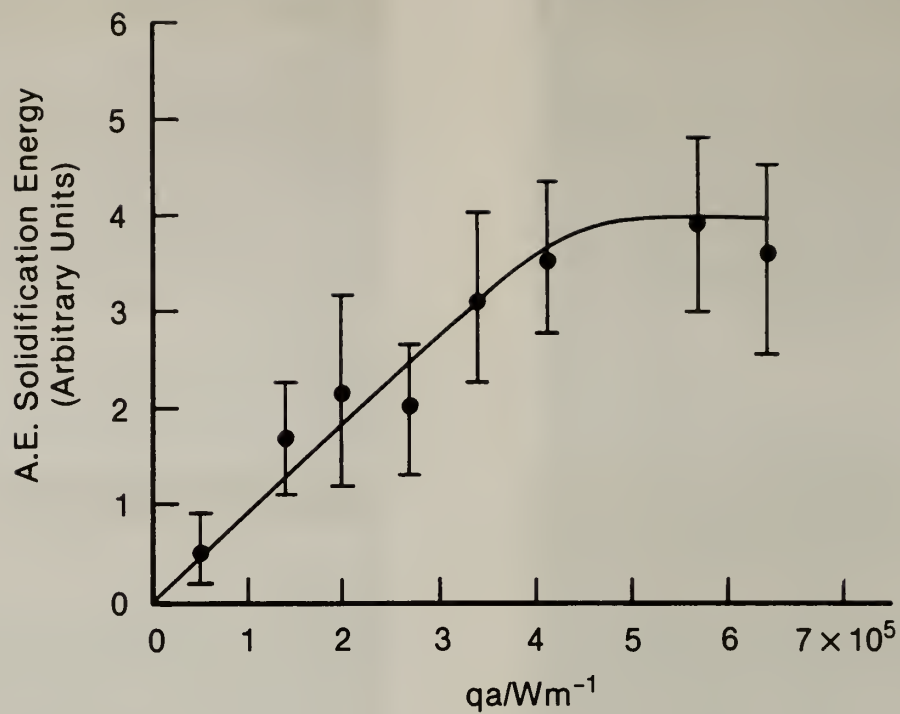


Figure 24 (a) Acoustic emission energy emitted during solidification (energy has same arbitrary units as figure 15a) and (b) Melt depth versus  $qa$  for 2219 aluminum.

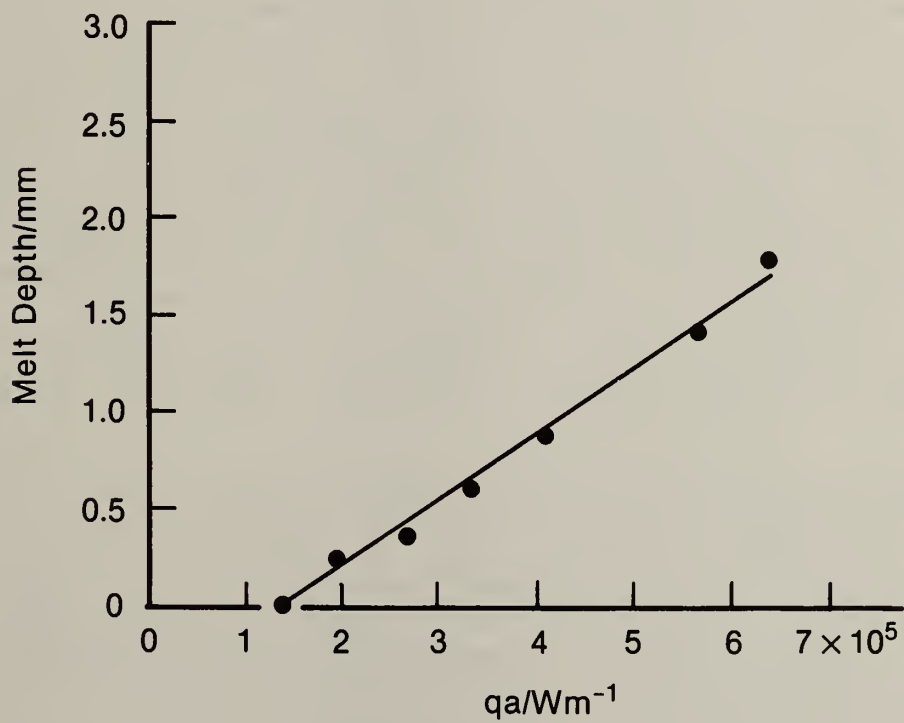
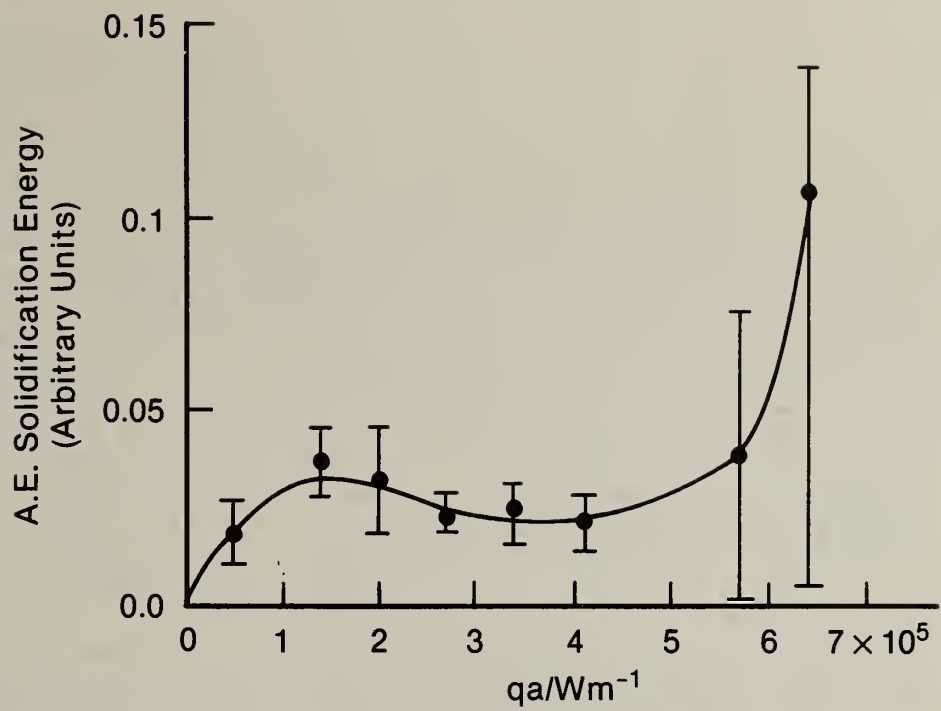


Figure 25 (a) Acoustic emission energy emitted during solidification (energy has same arbitrary units as figure 14a) and (b) Melt depth verses  $qa$  for 1100 aluminum.





## METALLURGICAL PROCESSING

### Task 12143

Metals processing research plays a central role in the Division's activities. The properties of alloys depend on their compositions and microstructures, which are dictated by their processing history. Thus, the effective performance of components in societal use depends strongly on solidification and solid state transformation processes, diffusion, and other kinetic changes that alloys undergo during production and shape forming operations. The central objective of this task is to develop data, measurement techniques, theory, and predictive models relating variables during metallurgical processing to microstructures, hence properties and performance of alloys. In addition, the Diffusion in Metals Data Center of the National Bureau of Standards is located in this group. This Center is a national metallurgical resource that provides a central source of extensive evaluated data on diffusion to the technical community at large.

A major development during 1982 was the obtaining of special funding from Congressional appropriations for new work on Metals Processing. Three million dollars were provided to NBS, for one year only, to develop new activities in rapid solidification and alloy coatings. These two technological fields show great promise of providing new and improved materials, which impart striking increases in strength, wear-resistance, corrosion-resistance and electric transformer efficiency. This funding has allowed establishment of advanced metals processing facilities that will be used as part of a continuing program to provide measurements, predictive models and standards needed for these technologies. Cooperation is being established with industry in which NBS will supply alloy samples for research, measure critical data, and provide guidelines to industrial designers who are developing new alloys. During the past year, numerous guest workers, industrial scientists, and distinguished visiting faculty members, such as Professor D. Turnbull of Harvard University, have come to NBS to participate in this program, for periods up to six months, and exchange information concerning these technologies.

Strong interactions have been developed with other Government agencies in these areas. New projects on rapid solidification and alloy coatings supported by the Defense Advanced Research Projects Agency and the Army Research Office have been initiated. The Proceedings of a National Workshop on Rapid Solidification held at NBS were published as an NBS report in December 1981. The purpose of this workshop was to provide coordination and guidance for the Government-wide program on rapid solidification and to determine means of involving industry more fully in this program. All Government agencies with significant programs in this field participated by providing overviews of their needs and plans for these materials. Major applications were discussed for rapidly solidified aluminum alloys, superalloys, ferrous alloys, and specialty materials, such as metallic glass. The workshop format then allowed response from industrial and academic representatives. These responses were summarized in the report. One recommendation of the workshop was that there was need for the establishment of facilities at NBS to provide workers in this field with rapidly solidified materials for research purposes, since these materials are often not otherwise available.

As a result of our current program, the metals processing laboratory has been significantly expanded and reorganized. Facilities now are available for study of all three major types of rapid solidification: powder production, ribbon production, and surface treatment. Work is being done on micropowder production by atomization, metallic glass production by melt spinning, and surface modification by electron beam melting and refreezing. A recent major addition to these facilities is a system for producing powders by electrohydrodynamic atomization techniques. Very fine droplets are formed with aid of an electric field. Upon rapid solidification of these droplets, submicron size powders are formed whose characteristics and microstructure can be examined to determine the effect of processing conditions on nucleation and solidification in individual particles.

A gas atomization system also is being constructed to produce larger sizes and quantities of rapidly solidified powders, which can then be consolidated to form bulk specimens. Consolidation will be achieved, for example, by a hot isostatic press that is being obtained. New alloy coating facilities being developed include a plasma-arc-transfer alloy coating system, a laser surface melting facility and improved alloy diffusion measurement equipment. The aim of this work is to produce quantitative measurements and understanding of rapid solidification and alloy coatings in order to provide predictive modeling and thus allow improved control of metal processes and products.

Rapid solidification studies are aimed at providing alloy designers with guidelines for control of these processes. As an example, measurements are being made of means of obtaining extended solid solubility. Experiments have been performed on Ag-Cu alloys using electron beam surface melting and melt spinning. At solidification velocities above 100 cm/s, considerable extended solubility has been obtained. These experiments use Ag-Cu as one of a broad class of alloys with a retrograde solidus, where enhanced solubility must be caused by a solute trapping mechanism. Predictive modeling is being used to relate solubility measurements to the  $T_0$  curve, which is the locus of compositions and temperatures where the liquid and crystalline solid free energies have the same value. Hence,  $T_0$  represents the highest interface temperature at which the partition coefficient can be unity. Obtaining special alloy properties characteristic of the single phase alloy thus depends on cooling the alloy rapidly below  $T_0$  before two-phase separation can occur.

In diffusion studies related to alloy coatings, the newly recognized phenomenon of diffusion-induced grain boundary migration is being investigated and measured. It is found that greatly enhanced mass transport useful for producing new improved alloy coatings can be obtained by this process. In particular, metals can be alloyed to surprisingly large depths from the surface without subjecting the coated sample to high temperatures. If high temperatures are avoided in the coating process, improved surface properties can be obtained without degrading the properties of the underlying bulk material.

In other areas of metals processing, new signal-processing techniques have been developed to improve signal-to-noise ratios during in situ ultrasonic measurements of solidification interface positions and velocities.



This result is important for ultrasonic monitoring and control of continuous casting of polycrystalline alloys, where reflections from grain boundaries are important. Convection produced during directional solidification is being measured and related to predictive models. Surface tension measurements in liquid alloys have been related to surface segregation effects in these melts. In making such measurements, techniques were developed which for the first time allow application of Auger methods to determine liquid alloy surface segregation with direct comparison to surface tension. As part of the continuing Diffusion in Metals Data Center effort, a computerized bibliographic reference system has been put into operation to allow improved retrieval of diffusion information.

Task members are currently active in organizing a national conference on Rapid Solidification Technology; Principles and Technologies to be held at NBS in December 1982. During the past year, conference sessions were organized on diffusion processes and on materials processing in microgravity at international conferences held by the American Society for Metals and the Materials Research Society. Task members serve on advisory committees for the National Science Foundation, Solar Energy Research Institute, and the National Aeronautics and Space Administration; on boards of international journals on diffusion and crystal growth; and on working committees of the ASTM, AIME, American Society for Metals, and the National Materials Advisory Board, including chairpersonship of the NMAB committee on rapid solidification processing.

#### Metals Processing Laboratory Subtask 1 of Task 12143

W. J. Boettinger, F. S. Biancaniello, S. D. Ridder, R. J. Schaefer, and R. D. Shull

To accomplish the objective of the metals processing initiative in the Metallurgy Division, this laboratory has continued to be expanded to permit research into the processing-microstructure-properties relationship utilizing innovative processing methods. A strong thrust in the area of alloy powder formation and consolidation is underway as well as improvements in electron beam surface melting and melt spinning techniques.

A new metal atomizing chamber has been designed and is currently under construction. When complete, this device will be used to produce up to 50 kg of rapidly solidified alloy powder. The system has been designed to allow for various atomizing techniques and to maintain an inert environment throughout the atomizing and powder handling process. For the initial atomizing trials the system will consist of a vacuum induction tilt-pour furnace and inert gas impingement and atomization via an induction heated tundish. The bulk of the atomized powders will be collected in a separately removable, vacuum tight can mounted below the atomizing tower. The fine metal dust will be collected in a demountable cyclone separator. This collection system will allow us to recover and maintain a clean and inert atmosphere for all the powder produced down to submicron sizes. A hot isostatic press unit has been ordered for the consolidation of metal powders into near net shapes for property determinations.

Additionally, powders of various aluminum alloys have been produced by an electro-hydrodynamic method which forms and ejects small quantities of extremely fine ( $< 10\text{ }\mu\text{m}$  diameter) alloy powders. A major advantage of this method is that many of these particles are electron transparent and permit relatively easy characterization. This process has been used to study the solidification dynamics of metal alloys subjected to large amounts of undercooling before freezing occurs. The systems studied so far include Al-Fe, Al-Mn, Al-Si, Al-Ge, Al-Cu, and Al-Cr.

The electron beam surface melting facility has been further upgraded by the addition of a stepping motor, an oscilloscope, a deflection coil-beam current synchronization system, and new devices for characterizing the energy distribution in the beam. These additions have enabled us to more precisely characterize the melting parameters required to meet the objectives of investigations on many different alloy systems. For example, the equipment has been used to produce continuous amorphous surface layers for acoustic studies, remelting and consolidation of plasma-sprayed carbide layers on aluminum for improved abrasive wear resistance, rapidly solidified surface layers on steel for wear and microhardness study, and rapidly solidified surfaces on alloys of aluminum, silver-copper, and titanium for microstructural analysis.

A second, more sophisticated, vacuum melt spinning apparatus has been constructed for the preparation of metallic alloy ribbons formed by cooling the alloy from the liquid state at rates approaching  $1\text{ M}^\circ/\text{s}$ . Such fast liquid quenching has been demonstrated to be responsible for the creation of metallic glasses and metastable crystalline alloys. Investigations of the morphology and structure of these quickly solidified materials, with particular attention devoted to the effects of variations in processing parameters, are presently being conducted.

#### Rapid Solidification

##### Subtask 2 of Task 12143

W. J. Boettinger, S. R. Coriell, R. J. Schaefer, and J. W. Cahn

This project is focused on increasing knowledge of the kinetic processes which occur during the rapid solidification of alloys. A broad class of experimental results on rapidly solidified materials are difficult to understand because existing theory needs extension to higher solidification velocities and because accurate quantitative experiments are difficult to perform due to the high cooling rates and small specimen sizes. The current work of this project investigates: (1) the solidification conditions required to produce material free of microsegregation and having solubilities for alloying elements in excess of the equilibrium amounts; and (2) the effects of nonequilibrium interface kinetics on solidification theories. Summaries of progress in these areas are reported below.

#### (1) Microsegregation and Extended Solubility

Electron beam surface melting experiments have been performed on a series of Al-based alloys with the goal of determining the conditions of absolute stability, and a series of Ag-Cu alloys with the purpose of determining the conditions for extended solubility.



## Al-Based Alloys

During the resolidification of an alloy following electron beam surface melting, the solid-liquid interface experiences a sequence of conditions of growth velocity and temperature gradient, depending upon the specific mode of melting. It has been found that in many cases this sequence of conditions can completely bypass the range of conditions where steady-state morphological stability analysis predicts an instability leading to cellular solidification. At some stages the planar interface is stabilized by high temperature gradients while at other stages the gradients in the liquid may be very small but the interface moves sufficiently rapidly to experience absolute stability due to surface energy. The latter regime is of particular significance, because it represents a drastic departure from the behavior expected by a mere extrapolation from lower velocity behavior.

An analysis of the influence of various metallic solutes on the solidification of aluminum has shown that the phenomenon of absolute stability is expected to occur at relatively low solidification velocities, or high solute concentrations, in samples containing manganese as the only solute. However, it is also clear that only small concentrations of certain impurities with small solute partition coefficients are required to upset this absolute stability and produce a cellular solid-liquid interface. It was found that aluminum-manganese without detectable cellular structure could be produced by the rapid solidification following electron beam surface melting of chill-cast samples in which a conventional cellular structure was present, but that the concentrations at which this could be attained were lower than predicted. Current efforts are directed toward techniques of surface preparation prior to electron beam melting to reduce the possibility of local contamination.

## Ag-Cu Alloys

The extension of solid solubility by rapid solidification is common, yet the relationship between alloy composition, growth rate, and thermodynamic constraints has not been significantly investigated. The system Ag-Cu has a particularly simple thermodynamic basis and a full metastable phase diagram including  $T_0$  curves has been calculated by Joanne Murray as part of the Metallurgy Division phase diagram activity. Of particular interest is the appearance of a retrograde solidus for both Ag and Cu solid solutions indicating that extension of solubility beyond the respective retrogrades must be accomplished by solute trapping.

A series of experiments has been performed with compositions between pure silver and the eutectic composition using electron beam surface melting of  $\sim 1$  mm wide weld strips at velocities between 1 cm/s and 200 cm/s. In these experiments the growth velocity is simply related to the e-beam traverse rate by a geometrical factor related to the weld puddle shape, which can be determined from metallography. Considerable effort has been expended on developing a method for preparing samples for electron microscopy from the surface melted



alloys. Alloy compositions which are dendritic or eutectic at growth rates of 1 cm/s become single phase, segregation free at growth rates (depending on composition) of  $\sim 100$  cm/s. For alloy compositions beyond the equilibrium solubility limit, this structure indicates solubility extension. For these alloys an interesting structure of bands of high and low copper content develops normal to the growth direction at intermediate velocities. The measurement of velocities required to produce extended solubility should for the first time, permit the evaluation of various theories for extended solubility by rapid solidification.

## (2) Interface Kinetics

Significant departures from local equilibrium at the crystal-melt interface can exist for solidification at rapid rates. Perhaps, the highest measured crystal growth velocities (50 m/s) are those of Ni dendrites growing into pure undercooled melts as reported by Walker and Colligan and Bayles. Recent theoretical (Langer and Muller-Krumbhaar) and experimental (Glicksman et al.) advances in our understanding of dendritic growth allow accurate calculation of the heat transport limited rate of dendritic growth as a function of melt undercooling. Inclusion of interface kinetics into the heat transport model of dendritic growth has been performed in collaboration with Professor David Turnbull to extend the model to high solidification velocities. We have used previous results on the effect of interface kinetics on the morphological stability of a solidifying sphere to calculate the effect of interface kinetics on the dendritic tip radius and hence the growth rates. An interface kinetic coefficient based on the estimated velocity of sound in molten nickel, provides a good fit to the dendritic growth data at high velocities as a function of melt undercooling.

Recent advances in the technology of rapid solidification, e.g., laser or electron beam melting and refreezing of thin layers on substrates, as well as the observed absence of microsegregation in many rapidly solidified materials has focused increased attention on the phenomenon of morphological stability at rapid solidification rates. The theory is used to determine the conditions under which a planar solid-liquid interface is stable to small perturbations and hence when microsegregation does not occur. Of particular interest is the fact that the theory predicts absolute stability --i.e., stability for any solute concentration and any positive temperature gradient--provided that the velocity exceeds some critical (high) value.

In collaboration with Professor R. F. Sekerka, linear perturbation theory was used to study morphological instability for rapid directional solidification at constant velocity under conditions where there is significant departure from local equilibrium at an initially planar solid-liquid interface. One of the more dramatic manifestations of the departure from equilibrium at rapid rates is the nonequilibrium partitioning of solute as may be characterized by a nonequilibrium value of the distribution coefficient  $k$ , which is the ratio of solute concentration in the solid to that in the immediately adjacent liquid from which it freezes. For example, measured values of  $k$  for silicon have differed by orders of magnitude from the equilibrium value for solidification rates of the order of a few meters/second and such differences would be expected to have a dramatic effect on morphological stability.

One way of attempting to account for the effect of a nonequilibrium value of  $k$  on morphological stability would be simply to substitute the value of  $k$  measured at the velocity for the unperturbed state into the classical analysis. In fact, the critical value of the velocity for absolute stability is proportional to  $k^2/(1-k)$  so a big effect might be expected. However, such a procedure of substitution of the actual value of  $k$  is not strictly correct.

Under conditions where the segregation coefficient  $k$  depends significantly on velocity  $v$ , the stability criterion depends explicitly on both  $k$  and  $\partial k/\partial v$  and instabilities that are oscillatory in time can occur for solute concentrations that are much smaller than those that would be necessary to cause nonoscillatory instability for the same  $k$  if  $\partial k/\partial v$  were simply neglected. Such oscillatory instabilities seem to be related to a "solute pump" mechanism according to which local changes in  $k$ , due to periodic changes in local interface velocity  $v$ , can occur out of phase with local interface position, thus resulting in lateral inhomogeneity of concentration on a length scale large enough that the resulting instabilities will not be suppressed by capillarity. Such instabilities can, however, be suppressed by a sufficiently large dependence of interface undercooling on  $v$ . When present, oscillatory instabilities lead to a three-dimensional segregation pattern in which periodic solute variations in the two transverse directions are modulated by a periodic variation in the direction of growth.

#### Diffusion-Induced Grain Boundary Migration Subtask 3 of Task 12143

J. R. Manning, D. B. Butrymowicz, and J. W. Cahn

In metallic systems, there is clear experimental evidence that grain boundaries can be induced to migrate under certain conditions when substitutional solute atoms are diffused along the boundaries. The formation of alloyed zones by diffusion-induced grain boundary migration has been observed at relatively low diffusion temperatures under conditions where lattice diffusion is essentially frozen out but where appreciable diffusion transport along grain boundaries occurred. This effect has been measured quantitatively in Cu-Zn and Cu-As in recent work on this project. Copper specimens were exposed to Zn or As vapor from  $\alpha$ -phase alloys. Diffusion into the grain boundaries caused migration of these boundaries and deposition of alloying elements in the regions traversed. Large surface alloyed regions were formed, which effectively provided alloy coatings in the regions through which the grain boundaries had migrated. The objective of this work is to establish the mechanisms and critical parameters controlling this phenomenon and thus provide predictive models for this process.

Electron microprobe composition profiles and area composition scans of these specimens show sharp step-like discontinuities in alloy composition at the edges of the alloyed regions. Each alloyed region is bounded on one side by the final position of the grain boundary and on the other side by the initial position of the grain boundary. This effect has been observed both in a hydrogen atmosphere which excludes oxygen from the sample and under conditions where on appreciable amount of oxygen



enters the region being alloyed. Close control of the vapor and of alloying conditions does not seem necessary to produce this phenomenon. Hillocks were observed to form on Cu-As samples, indicating that stresses are being generated, probably as a result of Kirkendall fluxes along the grain boundaries.

Theoretical models are being developed to explain the effects being observed. Current attention is focused on models that produce grain boundary migration as a result of climb of grain boundary dislocations. It is presumed that the alloying elements, Zn and As, diffuse along the copper grain boundaries faster than copper does itself. Thus, at temperatures where grain boundary diffusion can occur, there is a net flux of atoms into the boundaries. Grain boundary dislocation climb can absorb these additional atoms, but such climb will cause the boundaries to migrate normal to themselves. The migrating boundaries then should leave behind alloyed regions in the areas traversed, as is observed.

If a sharp concentration gradient is maintained at the leading edge of the boundary, the diffusion potential down the boundary can be maintained, thus providing steady state migration. The experimental observation that the solute composition of the alloyed regions in CuZn and CuAs does not decrease as migration proceeds, and may even increase somewhat, is consistent with this theory. This theory also may explain why diffusion-induced grain boundary migration has not been observed in ceramics. To preserve charge neutrality in ionic ceramic materials, Kirkendall fluxes of both anions and cations would be required to allow migration. Conditions for diffusion-induced grain boundary migration thus would be more difficult to obtain in ceramics than in metals, where a diffusion potential for only one species is required.

Diffusion-induced grain boundary migration is important not only for alloying but also for leaching, since much the same phenomena are observed to occur for de-alloying (unmixing) as for alloying (mixing). Either mixing or unmixing can occur, depending on the sign of the diffusion potential maintained in the particular experiment. These processes influence cellular precipitation and also have been observed in other solid-solid phase transformations involving diffusion couples. Applications have been made to fabrication of thin film electronic devices and control of degradation in metal contacts.

#### Diffusion in Metals Data Subtask 4 of Task 12143

D. B. Butrymowicz, J. R. Manning, and R. M. Hayes

Knowledge about the motion of atoms in alloys is important for studies of phase transformations, surface alloying to form coatings, oxidation rates, and many other phenomena dependent on mass transport in the solid state. An understanding of the parameters that control the rates at which these processes occur provides part of the basis for innovative development of new materials and control of their behavior. The NBS Diffusion in Metals Data Center provides a unique central source where data from the world's technical literature on diffusion and related kinetic processes are collected, evaluated, and then made available to



the industrial and academic communities. More than 25,000 documents reporting diffusion data now comprise the Center's database.

Automation of the bibliographic and classification files is being carried out to make the information contained in these reference files more easily searchable for locating specific data and more publicly accessible to the technical community. The documents on file have been classified and indexed according to the alloy systems and diffusion processes on which they contain data. This information along with bibliographic information is being processed into computer-readable form. A database management system has been designed and tested to allow entry of this information in an on-line computer available for automated searching by alloy compositions. Ability to obtain special types of diffusion information listed according to keywords also will be provided by this computerized system. This type of information base is important for evaluation of mass transport data. Studies of diffusion in grain boundaries and in iron-nickel-chromium alloys are currently being undertaken. This work forms part of a larger effort to develop a more complete data base for metals processing applied to critical materials.

Evaluation activities relating to technologically important copper alloys have resulted in a handbook of critically evaluated data prepared for the International Copper Research Association (INCRA). A camera-ready copy of this 500 page volume was delivered to the industrial research association as part of a cooperative agreement funded by the copper industry. This work will be published as part of the INCRA Metallurgy of Copper Series.

Ultrasonic Measurement of Solid/Liquid Interface Position during Solidification and Melting of Metals  
Subtask 5 of Task 12143

R. L. Parker

Ultrasonic techniques are being developed to provide real-time, in situ, nondestructive measurement of the position, velocity, and shape of solidification interfaces in opaque materials. The use of pulse-echo ultrasonic flaw detectors to detect the presence and location of cracks, voids, and other flaws in metals and nonmetals is well known. The solid-liquid interface in a melting or freezing metal can also be considered as a defect, in that there is a measurable difference in both sound velocity and density across the interface. For normal incidence of longitudinal waves in a typical case, about 10 percent of the pressure amplitude of the incident wave would be expected to be reflected. Thus, such a technique could be considered as a method for measurement, feedback, and closed-loop process control in such applications as continuous casting of metals.

A paper on this subject was presented at the First Conference on the Applications of Physics in the Steel Industry, October 5-7, 1981 at Lehigh University, Bethlehem, PA, which was jointly sponsored by the American Iron and Steel Institute and the American Physical Society. The proceedings of this Conference have been published by the American Institute of Physics, May 1982. In this paper are summarized our ultrasonic

pulse-echo measurements on the unidirectional solidification of tin in a Bridgman furnace; our ultrasonic pulse-echo measurements on large-grain 304 stainless steel at room temperature, demonstrating signal enhancement by computer spatial averaging in the presence of strong Rayleigh grain scattering; and a survey of earlier published work.

Current NBS work is focused on the study of the measurement factors inherent in possible use of the method for process control, as well as possible use for interface characterization; the latter use may be termed "ultrasonic metallography." The former use, process control, is important in the steel industry. For example, in continuous casting of steel, it would be useful to know at all times whether the solid skin thickness is sufficient to withstand the hydrostatic head of perhaps 10 meters or more of liquid steel, in order to forestall breakouts. Such breakouts can occur several times per year in such a caster, and they can be quite costly in repairs and reduced productivity. In order to make ultrasonic measurement of the skin thickness in a steel continuous caster, one must be able to do four things: couple an ultrasonic signal to the steel surface, propagate it to the solid-liquid interface (mushy zone in the case of alloys), obtain an echo from that interface, and identify the echo return in the presence of substantial noise from Rayleigh (grain) scattering. In the paper referred to above, the signal identification by computer enhancement was determined; and current work by others on EMATS transducers using noncontact Lorentz-force generation of ultrasonic pulses in hot steel billets appears to have solved the first (coupling) problem.

To examine the ultrasonic propagation through very hot steel and reflecting from the solid-liquid interface, an RF-induction furnace, capable of melting steel in an unidirectional (Bridgman) geometry, in an argon atmosphere, while coupled to a conventional transducer, has been designed, constructed and put into operation.

Using 1 MHz and 2.25 MHz longitudinal waves, we have made preliminary determinations of the solid-liquid interface location in 304 stainless steel rods, in the presence of substantial grain growth and its resulting attenuation, as well as absorption from other mechanisms (also some tests on carbon steel). One may consider the propagation and reflection measurements as analagous to measurement of the (frequency-dependent) transmission (T) of an electrical filter:  $T_p(\omega) \cdot T_r(\omega)$ . In the case of grain growth and interface motion, these two functions are time-dependent, too. Their measurement is essential for proper application of this measurement technique to industrial use.

#### Surface Tensions and Their Variations with Temperature and Impurities Subtask 6 of Task 12143

S. C. Hardy

Components of a bulk liquid phase which have low intrinsic surface tensions will preferentially segregate at free surfaces. Although the thermodynamics of this surface adsorption phenomenon was developed by Gibbs over a hundred years ago, many questions remain unanswered about details of the process such as the distribution of the adsorbed species



in the surface region and the interactions between coadsorbing species. Adsorption can produce large surface tension reductions and, in some situations, surface tension gradients which generate fluid flows. The resulting mass and heat transport are important factors in a number of procedures involving materials processing.

Although the study of adsorption at liquid surfaces is an active field of research, there have been almost no applications of modern surface analysis techniques to liquids. We have started a program of such studies of the surfaces of low vapor pressure metal alloys using Auger electron spectroscopy combined with classical sessile drop surface tension measurements. Our initial work has been with the Ga-Sn system. The Sn was found to be strongly adsorbed at the surface. Calculations of surface concentrations from the Auger measurements require knowledge of inelastic mean free paths and back scattering factors for the Auger electrons. Using recent theoretical calculations of these quantities for Ga and Sn, the surface composition of the alloys was determined from the measured Auger electron line amplitudes. The surface concentrations of Ga and Sn were found to be substantially in agreement with surface concentrations deduced from thermodynamic data assuming all the adsorption is in the top layer. This result supports the monolayer model of surface adsorption for the Ga-Sn system.

#### Convection During Directional Solidification Subtask 7 of Task 12143

R. J. Schaefer and S. R. Coriell

This research is directed toward an understanding of the fluid flow and solute segregation which occur during solidification. The nature of the fluid flow, its effect on the shape of the crystal-melt interface and the resulting distribution of solutes is examined. In particular, the role of solutal convection (gravity driven flow due to solute gradients) during the vertical directional solidification of a binary alloy is being studied both theoretically and experimentally. Solutal convection affects the microstructure and chemical homogeneity of directionally solidified alloys, and hence essential properties and performance such as fracture and corrosion.

Previous theoretical work [1] on solutal convection has shown that convective instabilities can occur at very low solute concentrations, e.g., 10 ppm for the solidification of lead alloys containing tin. Previous experimental work [2], on the growth of lead-tin off-eutectic alloys has established that solutal convection can cause extensive macrosegregation and prevent the growth of aligned composites. Our present effort is to develop a detailed understanding of the fluid flow which occurs during directional solidification, and to develop predictive models for macrosegregation and solute redistribution.

Experimental study of convection during directional solidification has used succinonitrile with and without small additions of ethanol. In this system the solid-liquid interface can be viewed directly and convection can be measured by tracking the motion of small particles suspended in the liquid. It is found that even in high purity material a convective



flow field is present due to radial temperature gradients induced by heat losses and by the influence of the container walls. These radial gradients result in a non-planar interface: when solute is present the resulting convective flow leads to the development of a macroscopic depression in the central region of the solid-liquid interface, which subsequently becomes the site of interface breakdown into a conventional cellular structure. By adding auxiliary heating in the region surrounding the interface, the thermal convection can be suppressed and the formation of the macroscopic depression and subsequent cellular structure is avoided. Thus, convective effects of a purely thermal origin dominate in this system unless special precautions are taken, but true solutal convection effects may be observable when the thermal convection is suppressed by properly designed auxiliary heaters. The overall decomposition of the solid-liquid interface into a cellular structure takes place at approximately the solidification velocity and solute concentration predicted by the stability theory. Details of the experimental observations and theoretical calculations for succinonitrile-ethanol mixtures have been reported [3].

In collaboration with R. G. Rehm and G. B. McFadden of the Mathematical Analysis Division, a theoretical model of double diffusive-convection during directional solidification of a binary alloy is being developed for low Prandtl number melts (metals and semiconductors). The nonlinear partial differential equations of fluid flow together with equations for temperature and concentration are solved numerically. The spatial variation of the solute concentration in the solidified alloy is evaluated from the numerical results.

In collaboration with R. F. Boisvert of the Scientific Computing Division and M. E. Glicksman and colleagues at Rensselaer Polytechnic Institute, the stability of the flow between two vertical, infinite, rigid, coaxial cylinders held at different temperatures, has been analyzed by linear stability theory. For a Prandtl number of 22.8 and a radius ratio of 0.02, the flow is unstable to an axisymmetric perturbation at a critical Grashof number of 2150; the wave speed of the instability is comparable to the maximum velocity of the unperturbed flow. When the rigid outer cylinder-fluid interface is replaced by a crystal-melt interface which can change shape, two new modes of instability occur at lower Grashof numbers. There is an asymmetric instability with a critical Grashof number of 180 and an axisymmetric instability with a critical Grashof number of 460; for both of these modes the wave speed of the instability is several orders of magnitude smaller than the unperturbed flow velocity.

These calculations were motivated by and are in general agreement with recent experiments at Rensselaer Polytechnic Institute on succinonitrile. A long vertical cylindrical sample of succinonitrile was heated by an electrical current through a coaxial vertical wire so that a vertical melt annulus formed between the coaxial heater and the surrounding crystal-melt interface. Above a critical Grashof number of circa 200, a helical crystal-melt interface formed which rotated steadily about the cylinder axis; the wave speed was several orders of magnitude less than the base flow velocity. These experiments demonstrate a crystal-melt interface instability under conditions for which in the absence flow, the crystal-melt interface would be morphologically stable.

- [1] Coriell, S. R.; Cordes, M. R.; Boettinger, W. J.; Sekerka, R. F. J. Crystal Growth 49: 13; 1980.
- [2] Boettinger, W. J.; Biancaniello, F. S.; Coriell, S. R. Met. Trans. 12A: 321; 1981.
- [3] Schaefer, R. J.; Coriell, S. R. Materials processing in the reduced gravity environment of space, Guy E. Rindone, ed., Elsevier, 1982, p. 479.





## MECHANICAL PROPERTIES AND WEAR

### Task 12144

This task addresses measurements and standards needs concerned with the application of metals to wearing situations, and also to their use as synthetic implants in humans. Specific projects are described below and are concerned with various modes of wear, the mechanisms involved, the effect of metallurgical parameters, the need for improved measurement capabilities, and the provision of standards and reference materials.

The importance of wear to U.S. industry and technology has only been appreciated fully in recent years. Studies indicating the costs of wear have been conducted in three countries (U.S. costs are estimated at \$30 B to \$50 B per year) and those results have led to increased Government and private emphasis of wear control and wear research. Most of the work on wear in this task resulted from an expanded NBS program in FY80 through the new Durability initiative. NBS has a unique opportunity in this field to provide help to the industry in standards and measurements areas, as well as to contribute to an improved basic understanding of wear. One area of current industrial interest involves coatings applied to metals for improved wear (and corrosion) performance. More widespread use of coating technology can conserve critical materials (by reducing their use in bulk alloys) and can improve productivity by efficient use and reuse of existing designs and components. However, the state of understanding of wear of thin metal coatings is not well advanced. Methods for accurate wear testing of very thin coatings are not adequate. These and other related needs are important technological questions for NBS to address in the wear area; in fact, a new budget initiative this year on Metals Processing includes work on the wear performance of metals coatings.

Highlights of this year's activities include the provision through the Office of Standard Reference Materials (OSRM) of a reference material for conducting abrasive wear tests, the development of an ASTM standard method for solid particle erosion testing, results on the galling wear of a number of alloys, and studies of the break-in process in copper alloys and aluminum alloys. One staff member is now Chairperson of ASTM Committee G2 on Erosion and Wear, and Vice-Chairperson for the 1983 International Wear Conference to be held in Washington next April. Two guest workers participated in our activities this year from the University of Virginia, developing a new theory of wear emphasizing materials effects. Two invited talks were given at the Gordon Research Conference on Wear this summer by staff members. A one day symposium on microhardness-related research was organized by a staff member and held at NBS during May; it involved nine technical papers in this subject area.

The work on metallic surgical implant materials in this task covers a number of different studies including corrosion, fatigue, metal ion/protein reactions, surface modifications, interfaces, and standards. Biomaterials research has been a rapidly growing scientific effort throughout the world over the past 15 years; as a result, hundreds of thousands of people have benefited. This trend continues as improvements which are possible through advancing materials technology are made. The purpose of this NBS work is to provide measurement methods, material property

data, and standards which are necessary for improved design, materials, and quality control of metal implants. There is considerable interest in the work done at NBS in this area; this is evidenced by many scientific interactions, information requests, and invited talks to industry, universities, and other groups. Staff members actively participate on the ASTM Committee F4 on Medical and Surgical Materials and Devices. This past year saw the establishment of recommended tests for wear and for corrosion. Both of these can be used for material tests in much needed device performance standards. We are the coorganizer of the Second ASTM Symposium on the Corrosion and Degradation of Implant Materials to be held in Louisville, KY, May 1983. NBS will also handle arrangements for the Second World Congress on Biomaterials which is to be held in Washington, DC, in April 1984.

The task is divided into four subtasks whose activities and accomplishments over the past year are described next. These subtasks are Metallic Wear, Lubricated Wear, Wear Standardization and NDE, and Metallic Biological Implant Materials.

#### Metallic Wear

##### Subtask 1 of Task 12144

K. J. Bhansali, P. J. Blau, L. K. Ives, F. Matanzo, S. Nutt, C. Olson, and A. W. Ruff

This subtask consists of several projects concerned with the wear and friction of metals. Studies are carried out of metal-to-metal wear under clean conditions, and of metal wear under abrasive conditions. The emphasis is on precise, meaningful measurements of wear and friction, and on an improved understanding of wear mechanisms and the role of metallurgical parameters. Wear studies are carried out in the laboratory under carefully controlled conditions, in order to draw valid conclusions about the mechanisms involved.

Composites of aluminum alloys with particles of chromium carbide have been made by surface alloying methods. It was hoped that a better interfacial bond between the hard carbides and soft aluminum matrix could be achieved over the usual solidification approach for composites involving silicon carbides. The different affinity for carbon is believed to be greater between chromium and aluminum than between silicon and aluminum. Hence, formation of a weak aluminum carbide phase at the interface between silicon carbide and aluminum is more likely than at the interface between chromium carbide and aluminum. Abrasive wear tests were conducted on these composites. Results of the tests look very promising as shown in figure 1. SEM examination of the wear scar region indicates a good bond between the chromium carbide particles and the matrix. This work is being prepared for publication.

Investigations of the influence of metallurgical parameters on the threshold galling stress also have been conducted, using the galling wear tester built last year. A series of Fe-Mn-Si alloys with controlled variations in stacking fault energy (SFE) were obtained (supplied by ARMC0) to explore the relation to galling threshold stress. The influence of additions of alloying elements like Pb and Sn on the galling of brasses was evaluated. The ratio (R) of threshold galling stress to penetration



hardness was used to evaluate relative galling tendencies of alloys. For pure copper R is 0.007 whereas for 70 to 30 brass it is 0.048. This increase in relative resistance to galling is believed to be due to lower stacking fault energy of 70 to 30 brass compared to that of copper. No galling has been observed so far in lead or tin bearing brasses up to R values of 0.2. Such an excellent resistance to galling of lead or tin bearing brasses is believed to be due to their poor shear strength owing to the presence of a lead- or tin-rich phase at the grain boundaries. Temperature is also believed to have a considerable influence on cross slip of dislocations and hence on galling behavior. A modified sample holder was designed and built to study galling behavior above room temperatures, up to about 700 °C, in the coming year.

In another project a wet sand abrasive wear test machine was modified to also include normal force and frictional force measuring capabilities. A project to study the effect of heat treatment of a 1090 steel on its abrasion resistance using this wet sand abrasion tester, and also the dry sand abrasion tester, has been initiated. A change in relative wear ranking due to corrosion affects under wet conditions is expected.

A new project to investigate the effect of residual stress on abrasive wear has been initiated jointly with the University of Notre Dame. A system to measure the residual stresses using a blind hole drilling technique was purchased and loaned to the University of Notre Dame. Preliminary measurements there indicate that a definite residual stress pattern is generated during dry sand abrasion testing. It is believed that prior residual stresses may be removed during the initial wear-in period and a steady state residual stress pattern is then established. This will be studied further in the next phase. In addition, the effect of pre-stress on the abrasive wear of carbide-containing alloys will be investigated.

In another project, investigations have continued on the influence of microstructure and different wear modes on the friction and wear running-in behavior of Cu-Al based alloys. In addition to the binary single phase alloys studied in the previous year, two commercial alloys (CDA 638 and 688 bronze) and a polyphase Cu-12 wt. % Al alloy were tested for unlubricated running-in behavior on the computer controlled block-on-ring (52100 steel rings) tribometer. In the commercial alloys, compositional difference effects on friction coefficient changes during running-in were quite pronounced. Part of these observed differences may relate to the different balance of competing wear modes identified in post-test microstructural studies of CDA 638 and 688 surfaces. Heat treatment effects on wear of the Cu-12 wt. % Al alloy were also investigated. The martensitic condition of this alloy gave not only lower hardness, but also lower wear loss compared with the more equilibrium, two phase eutectoid microstructure produced by a different heat treatment. Further effects of heat treatment on both wear and friction of the Cu-12 wt. % Al alloy are to be investigated in the next year.

Work is nearing completion on construction of a controlled atmosphere tribometer with high vacuum capabilities. Within the next four months, computer interfacing of the device should be completed. Studies of surface contamination effects and controlled atmospheres on long-term



transitions in wear mode and on running-in behavior are planned, to isolate the influence of combinatory factors responsible for net friction and wear values. Changes in the contact conditions during the tests (particularly the gas atmosphere composition) are also planned for systematic study.

Another project concerns the wear of HSLA steels having high ductility, the so-called dual-phase steels. Five alloys have been studied along with tool steel and low carbon steel under dry sliding conditions against 52100 bearing steel. The extended ductility property of the DP steels does produce an increased wear resistance under these test conditions. In contrast the yield strength itself does not determine (or correlate with) the wear resistances. Two primary factors appear to determine the wear; environmental conditions (water vapor content) and alloy plasticity properties. Two basic types of wear debris particles are formed; small primarily iron oxide particles, and larger primarily metallic particles. These results are presently being prepared for publication. The experimental work was carried out with the assistance of Ximing Meng, a Guest Worker from China.

A new project this year is being carried out by a NRC-NAS-NAE postdoctoral fellow. It concerns microscopic studies of sliding wear on titanium. It is well recognized that titanium exhibits poor tribological properties, however, the basic reasons are not understood. Presumably, they involve the mechanical, thermal, and surface properties of the metal. This study is exploring the significance of slip system constraints, mechanical twinning vs slip deformation, and surface conditions on the wear and friction properties of titanium. Transmission electron microscope results from worn specimens will be described in a talk planned for the Electron Microscope Society Meeting this summer.

Work is continuing on the dry sliding wear studies of Ni alloy coatings on steel. Results from the previous study have appeared in the ASTM publication on Wear Testing of Coatings (see fig. 2). There it was shown that an amorphous alloy coating had good wear properties, and that the laminar morphology (composition banding) and precipitate strengthening effects in the heat treated alloy coatings were very significant features. The new work, jointly conducted with Dr. Lashmore of the Materials Chemistry Division, involves Ni alloy coatings containing small aluminum oxide particles. Presumably, this approach may increase resistance to abrasive-type wear and retain the good metal-to-metal wear characteristics.

Another project has been completed concerning the abrasive wear properties of laser surface-melted aluminum and titanium alloys containing particle additions of WC and TiC. Reductions in wear rates by a factor of 10 or more were found to result from this processing treatment. Studies of the effect of microstructure, particle type and size, and composition have been completed. A paper is being prepared for presentation at the Fourth International Conference on Wear of Materials, scheduled for April 1983 in Washington. This work has been done jointly with a scientist at the Naval Research Laboratory.

In a project concerned with basic wear processes, a microscratch hardness investigation of eroded copper specimens is being carried out

in a joint effort with Professor J. Moteff of the University of Cincinnati. The eroded copper specimens had previously been the subject of an extensive electron microscopy investigation in our laboratory to determine the relationship between microstructure and erosion conditions. Under mild wear or erosion conditions, the conventional microhardness test is not likely to be applicable as a means to study the resulting wear damage. A microscratch hardness method is being examined in this new work to determine if information can be obtained on the mechanical properties of surface layers which may be no more than a fraction of a micrometer thick.

In another project, transmission electron microscopy is being applied to reveal the microstructure of worn surfaces and wear debris. The recently acquired analytical electron microscope equipped with an x-ray energy dispersive spectrometer and an electron energy loss spectrometer has added a new dimension to this project. With this instrument, it has become possible to probe changes in elemental composition and crystal structure on a scale of a few nanometers. To take advantage of this capability it has become necessary to develop suitable specimen preparation methods. To this end, new procedures for preparing cross sections through worn surfaces and for removing thin surface layers have been developed. One area of particular interest in which electron microscopy has been applied concerns the study of microstructural changes brought about by plastic deformation during different kinds of wear. Fairly extensive wear and characterization studies on copper have been carried out in the past. The development of a dislocation cell structure and the formation of crystallographic texture were revealed in that work. Additional work on copper is planned to compare wear debris structure with subsurface structure. The microstructural studies are also being extended to other materials. The effect of stacking fault energy, crystal structure, and precipitation hardening are being investigated. Two commercial bearing steels, 52100 and carburized 4320, are being examined. Further, a new area of investigation concerns the nature of the microstructural changes that occur at the onset of scuffing. Scuffing is a severe form of wear in lubricated systems that is usually associated with failure of the lubricant film. Metallurgical factors, however, play a significant role in determining the conditions under which scuffing occurs.

#### Lubricated Wear

Subtask 2 of Task 12144

L. K. Ives, M. Peterson, J. Harris, and A. W. Ruff

An investigation of the lubrication and wear mechanisms of the solid compound  $\text{SbSb}_4$  has continued. This project is sponsored by the Office of Naval Research as part of a Navy program to develop lubricants with improved antiwear capabilities, better high temperature stability, longer life to reduce maintenance costs, and the ability to lubricate such difficult materials as titanium alloys and stainless steels.  $\text{SbSb}_4$  is the most promising of several compounds that were developed with Navy support by an industrial research laboratory. The compound was reported to impart a greatly improved load carrying capacity and



antiwear response in four-ball tests when blended into several conventional base greases. The mechanism by which  $\text{SbSbS}_4$  might show such improvements was not determined although it was suggested that being a solid material it might act as a solid lubricant, and indeed, comparisons were made with  $\text{MoS}_2$ . In order to study the solid lubricant characteristics of  $\text{SbSbS}_4$  a series of tests with steel specimen materials were carried out at temperatures ranging from 20 to 600 °C. At 20 °C a friction coefficient of 0.7 to 0.8 was obtained. As the temperature was increased, the coefficient of friction decreased to a value of about 0.4 at 250 °C and approached 0.2 at 500 °C. These changes in friction coefficient are associated with thermal decomposition and oxidation of  $\text{SbSbS}_4$  to form other compounds, chemical reaction with the steel surface, and the effect of temperature on the mechanical properties of the compounds present. The initial reaction as the temperature was raised above 20 °C has been determined to involve the release of sulfur and the formation of  $\text{Sb}_2\text{S}_3$ . There was no evidence in these studies that  $\text{SbSbS}_4$  or any of its compounds were effective solid lubricants in air at room temperature. The reduction in coefficient of friction does, however, indicate that compounds derived from  $\text{SbSbS}_4$  do exhibit some lubricant properties at elevated temperatures. Although it had been demonstrated that  $\text{SbSbS}_4$  is an effective lubricant additive at high contact loads and speeds, its performance might differ under less severe conditions, especially at low sliding speeds where thermal effects might be minimized. To study this regime a series of block-on-ring wear tests was conducted at a sliding speed of 5.5 cm/s and load of 267 N. The block and ring materials were 52100 steel. A comparison was made between lithium base grease and the base grease with additions of  $\text{SbSbS}_4$  and S. The results are shown in figure 3. Both S and  $\text{SbSbS}_4$  produced a significant but comparable reduction in wear. Electron microscopy studies on surface films removed from worn surfaces indicated that the formation of iron sulfides played a significant role in the reduction of wear. The film formed when S was used as an additive differed from that for  $\text{SbSbS}_4$ . With S the film was found to consist primarily of  $\text{FeS}_2$  while both  $\text{Fe}_{1-x}\text{S}$  and a layer of amorphous  $\text{SbSbS}_4$  were obtained when  $\text{SbSbS}_4$  was used as an additive. The significance of this finding is still being investigated.

Although experimental activities associated with the NBS Recycled Oil Program were concluded at the end of last year, there was a continuation of some activity into this year. In particular, an invited talk on the subject of wear tests for the evaluation of rerefined motor oils was presented at the Chicago Chapter of the American Society of Lubrication Engineers. Further, an invited paper summarizing results in our project to develop a wear test to evaluate motor oils will be presented at the Conference on Measurements and Standards for Recycled Oil-IV, scheduled for September at NBS.

#### Wear Standardization and NDE

P. J. Blau, L. K. Ives, F. Matanzo, and A. W. Ruff

One project involves the development and certification of a standard reference material (SRM) for use with the new Dry Sand/Rubber Wheel Abrasion Test (ASTM Standard G65-80). Approximately 250 specimens of D-2 tool steel, the material which was selected for this application,



have been prepared. Certification tests using NBS equipment have been completed and the statistical analysis and writing of the certification statement are expected to be completed this year. An additional 750 SRM specimens are being prepared for later issue. Publication of ASTM G65-80, Standard Practice for Conducting Dry Sand/Rubber Wheel Abrasion Tests, has evoked considerable interest among producers of abrasive wear resistant materials, manufacturers of equipment subject to abrasive wear, and users of these materials and equipment. The Dry Sand/Rubber Wheel wear test is especially applicable for ranking materials exposed to conditions involving so-called three-body abrasion as might be encountered in earth moving and agricultural equipment, in mining, and certain ore processing machinery. A Workshop sponsored by ASTM Committee G-2 on Erosion and Wear was held in June for the specific purpose of addressing problems which might be encountered in applying this Dry Sand/Rubber Wheel test, and to consider the influence that changes in various test conditions and parameters might have on test results. The importance of a suitable calibration specimen was clearly recognized during the course of this Workshop. We contributed one paper to the Workshop illustrating the effect of sand flow rate and moisture content on the wear rate using this test.

Another project is investigating the feasibility of using new metal processing techniques such as electron-beam (EB) surface melting and fiber melt spinning to produce microhardness standards. This work was supported by the Office of Standard Reference Materials and was conducted in conjunction with the NBS Electrodposition Group (D. Lashmore, Materials Chemistry Division). Electron-beam surface melting techniques developed in the Metallurgy Division processing laboratory were used on 440C stainless steel bar stock to see whether areas of sufficient homogeneity of microhardness suitable for low load micro-indentation testing (0.098 to 0.98 N loads) could be produced. Although the EB zones in the stainless steel were quite microstructurally uniform, electroformed Cu-based materials with a similar microhardness range showed much better reproducibility of microhardness numbers. The decision was made to produce electroformed Cu standards for this reason. Work continues on characterizing melt-spun ribbons of  $\text{Pd}_{80}\text{Ge}_{20}$  for possible use as standards in other microhardness number ranges. Additional work on characterizing heat-treated, electroformed Co-based materials for standards is planned for the coming year, also in conjunction with the Materials Chemistry Division.

One project supported by the Office of Standard Reference Materials concerns the development of standards for use with the ferrographic method of analysis of wear debris particles in lubricants. This method has proven itself as a viable condition monitoring tool; however, the quantitative capability involved needs improvement. After participating in several interlaboratory measurement rounds, it became clear that certain problems of precision and bias could be overcome if adequate standards were available. Development of an artificial sample of wear debris particles and a standard to be used for particle density measurements is now in progress, and should help to further quantify the overall method.

A project concerned with solid particle impingement erosion has completed the development of a test procedure that has been accepted by the ASTM

(Committee level). A final round of interlaboratory testing was also organized, conducted, and evaluated. Five laboratories participated. The new standard is the first for conducting erosive wear measurements under laboratory conditions in the U.S. The typical level of measurement precision within an experienced laboratory is 5 to 10 percent using this method.

Quantitative image analysis was employed in a project completed this year to aid in the development of standardized methods for characterizing the geometric shapes of sand particles for use in dry sand/rubber wheel (DSRW) tests. A perimeter ratio (PR) parameter was used to evaluate the variations in abrasive sand particle shapes in batches of sand used in testing over a several year period. These ratio parameters remained very constant from batch to batch in the rounded AFS 50-70 sand specified for the ASTM DSRW procedure. Sharper particles produced by crushing quartz and screening it to the same sieve size range as the AFS 50-70 sand had larger PR parameters to start with and produced greater amounts of abrasive wear on steel samples. Image analysis comparing both used and unused sand showed that the average PR parameters for AFS 50-70 and for crushed quartz remained relatively constant before and after the abrasion tests. However, there appeared to be increases in the standard deviations of PR parameters of both kinds of abrasives after use in DSRW tests. Further work is planned using a new image analysis system to investigate larger sample sizes and to more completely automate the shape classification procedure. This future work should improve the statistical significance of PR data by shortening the time required to analyze larger numbers of particles.

Another project is involved in applying acoustic emission detection methods to a study of metallic wear in order to monitor particular wear events such as subsurface crack growth (delamination). While the noise and vibration background in a typical wear test situation can be complex, it may be possible to remove such interferences in the detected ultrasonic signals using filtering, synchronous detection schemes, and computer based signal processing. A laboratory bench wear tester has been instrumented with an acoustic detection system and recorder. An incremental stressing contact geometry is used, and the anticipated emission events are searched for in synchronism with the load pulses. Three different steels having varying toughness have been studied; copper has also been examined briefly, all sliding under lubricated conditions against 52100 steel counterfaces. Some unusual emitted waveforms have been detected from the steel specimens, but they do not occur with every load pulse. Digital pulse recording and analysis will be tried next in order to obtain better resolution of the waveform details. This work is carried out in coordination with the other acoustic emission work in the Metallurgy Division concerned with signal analysis and source characterization.

#### Metallic Biological Implant Materials Subtask 4 of 12144

A. C. Fraker, G. J. Mattamal, A. C. Van Orden, and C. Olson

The work of this task covers a broad spectrum of activities as is necessary for investigations in the multidisciplinary field of biomaterials.



Studies during the past year have dealt with standards, interfaces, corrosion, corrosion-fatigue, metal ion/protein reactions, surface modification through ion implantation, and porous coated materials. These investigations are described briefly in the following paragraphs. The accomplishments in this task are made possible by the participation of other people in addition to the regular NBS staff. Other personnel associated with this task are Dr. M. Ashraf Imam, George Washington University and the Geotech Corporation, Dr. Pei Sung, Bureau of Medical Devices, the Food and Drug Administration, Dr. Kirk J. Bundy, the Johns Hopkins University, college students Alison Bailey (North Carolina State University) and Jacqueline Smith (Howard University) and student aides, Christine Schrider and Susan Nossal.

### Standards

There is a strong need to develop performance standards for medical and surgical devices. The test methods developed in ASTM, for example, for materials can be used for this purpose. This past year the ASTM F746-82, Standard Method of Test for Pitting or Crevice Corrosion of Metallic Surgical Implant Materials, was passed. NBS participated for many years with other university and industrial laboratories in developing this test and conducting interlaboratory tests. This is the first standard corrosion test for surgical implant metals, and it will be followed by the production of the NBS 316L stainless steel standard reference material (SRM) for use with the standard test. NBS has obtained 316L stainless steel for use as standard reference material from the supplier who furnished the round-robin specimens and who supplies implant manufacturers. Work on the SRM production is underway and some studies to refine the test are being conducted in terms of effects of solution oxygen content, solution pH and metal surface condition.

### Interfaces

Metallurgical studies of interface bonding on implant alloys are underway and are supported by the Bureau of Medical Devices, Food and Drug Administration. The purpose of this work is to determine the effects of surface treatments of metals on interface problems or strength of metal/polymethyl-methacrylate (bone cement) interfaces in joint prostheses. A review was conducted of over 200 articles relating to bone cement, cemented prostheses, forces involved in the loading of the hip joint and other prostheses installation considerations. This literature review suggests that there is a discrepancy between the calculated positions of maximum stress obtained by analysis and those positions where failure is most likely to occur clinically (at the interface). A hypothesis which could possibly explain this discrepancy is that horizontal forces in the hip have not been taken into account analytically. If they were it is thought that the results would indicate that high torsional stresses exist at the interface (see fig. 4). Thus, studies of the bone cement-metal interface in torsion are important. The numerous test methods of ASTM D-14 on adhesives were reviewed and found to be inappropriate for testing the bone cement/metal interface. An appropriate test method involving torsion loading was developed to the point of application for measuring bond strength of the cement/metal interface. This test has been upgraded and is being conducted this summer using a computerized commercial mechanical testing machine.



The results of the first year's work have been presented at technical meetings at the FDA, NBS, and The Johns Hopkins University. The annual report which was sent to the FDA is being published as an NBS Internal Report.

### Corrosion

Electrochemical measurements are made on implant metals using techniques of anodic polarization, localized corrosion stimulation, and repassivation. Studies were continued to investigate the effects of small compositional changes in Fe and Cr contents on the corrosion behavior of the Co-Cr-Mo implant alloys. Corrosion measurements were made in physiological saline solution at 37 °C. Repassivation measurements proved to be the most sensitive technique and showed that increased Fe content caused the alloy to have a slower repassivation rate. Analysis of the surface films using scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) showed the films on these alloys to be enriched in Fe, Si, and Mo. These data are especially significant when considering new standard specifications for composition of implant metal alloys. Varying or new processing techniques can introduce increased amounts of metals such as iron, and data are needed to show the effects of these changes. These data have been supplied to the ASTM F-4 Committee. These results were presented in talks at the Washington, DC, Bioengineering Colloquium; at the annual meeting of the Society for Biomaterials, Disney World, FL; and at the Electron Microscopy Society of American meeting in Washington, DC. Further corrosion studies on other implant alloys involving effects of proteins and details of repassivation processes are planned.

### Corrosion-Fatigue

An important requirement which load-bearing implant metals must meet is that of high corrosion-fatigue resistance. This is due to the repeated loading to which they will be subjected and to the aqueous saline environment. Experiments are conducted to determine the influence of microstructure and other designated variables on the corrosion-fatigue life of implant metals when tested under conditions of fully reversed torsion at a constant shear strain amplitude and a frequency of 1Hz in flowing physiological saline solution at 37 °C. Titanium alloys, Ti-6Al-4V and Ti-4.5Al-5Mo-1.5Cr have superior corrosion-fatigue behavior over the other implant metals under these testing conditions. Work on the effects of heat treating on phase composition, microstructure, and fatigue life of these alloys continues. This is a collaborative effort with the George Washington University. It was established several years ago that maximum corrosion-fatigue life for the Ti-6Al-4V is obtained by heat treating at 900 °C and rapidly quenching. However, this alloy still is used in the mill annealed condition for implant purposes. Recent corrosion-fatigue tests of this mill annealed alloy after the surface was sand blasted showed an increase in corrosion-fatigue life. This sand blasted material, if improperly heat treated, has very low-fatigue resistance. The Ti-4.5Al-5Mo-1.5Cr alloy is not an implant alloy but possibly could be used for this purpose. Corrosion-fatigue tests show that heat treating this material at 915 °C doubles the fatigue life over that resulting from five other heat treating temperatures. This is a

more complicated alloy than Ti-6Al-4V and heat treating procedures have not been completed to produce the optimum mechanical properties. This work is continuing. Other corrosion-fatigue studies are concerned with Co-Cr-Mo materials after different modes of processing (casting, forging, hot isostatic pressing, etc.) and with metal porous coated specimens.

### Metal Ion/Protein Reactions

Knowledge of the biological response to metal ions is essential for determining the suitability of a given metal or alloy for use as an implant. Corrosion data and chemical analysis results show that placing metals in the body results in some metal ion release. Some metals are indicated as being more harmful than others and nickel is in this category. Nickel is a constituent of 316L stainless steel, Co-Ni-Cr multiphase alloy and some other alloys which are used for implant purposes. Laboratory investigations involving  $Ni^{++}$  ion interactions with human serum albumin were carried out this year. An ultrafiltration method was used in which a filter entraps the protein with or without bound metal ions. This was coupled with atomic absorption chemical analysis techniques to determine the amount of nickel bound to the human blood serum albumin (HSA) molecule. Results indicated that HSA has approximately 15 identical and negligibly interacting binding sites for the  $Ni^{++}$  ion in the pH range of 5.6 to 6.3 in unbuffered solution at 37 °C. The pH has a strong influence on the  $Ni^{++}$  HSA interactions with increased binding affinity occurring with increasing pH in the pH range studied. These results were presented at the 1982 annual meeting of the Society for Biomaterials, Disney World, FL. Additional work is underway to obtain data on nickel ion reactions and to study other metal ion reactions as they occur or in the presence of other metal ions. Metal ion release from alloys mostly commonly will be a combination of several metal ions.

### Surface Modification

Titanium and titanium alloys have been ion implanted with boron, carbon, and nitrogen. This work is being conducted to determine if wear and mechanical properties of titanium can be improved without sacrificing the excellent corrosion resistance of titanium. Titanium specimens were bombarded at NBS with the B, C, and N ions to a dosage of  $1 \times 10^{17}$  ions/cm<sup>2</sup> and also at lesser dosages. Anodic polarization measurements of corrosion behavior showed some changes but no serious detrimental effects. Transmission electron microscopy and electron diffraction indicated a highly deformed surface layer. This work was reported at the October 1981 AIME meeting in Louisville, KY. Much work remains to be done relating to the properties and the preservation of the very thin surface film and this effort is continuing.

Porous metal coatings on metal substrates are being applied on prosthetic devices for the purpose of obtaining better fixation by ingrowth of bone and tissue. This fixation is appropriate for people with healthy bone. This investigation is being initiated to study corrosion-fatigue of the porous coated material to determine the corrosion behavior and to characterize the interface and the porous coating. This work is being conducted in cooperation with a local company, the Artech Corporation which applies the arc plasma sprayed porous coatings.

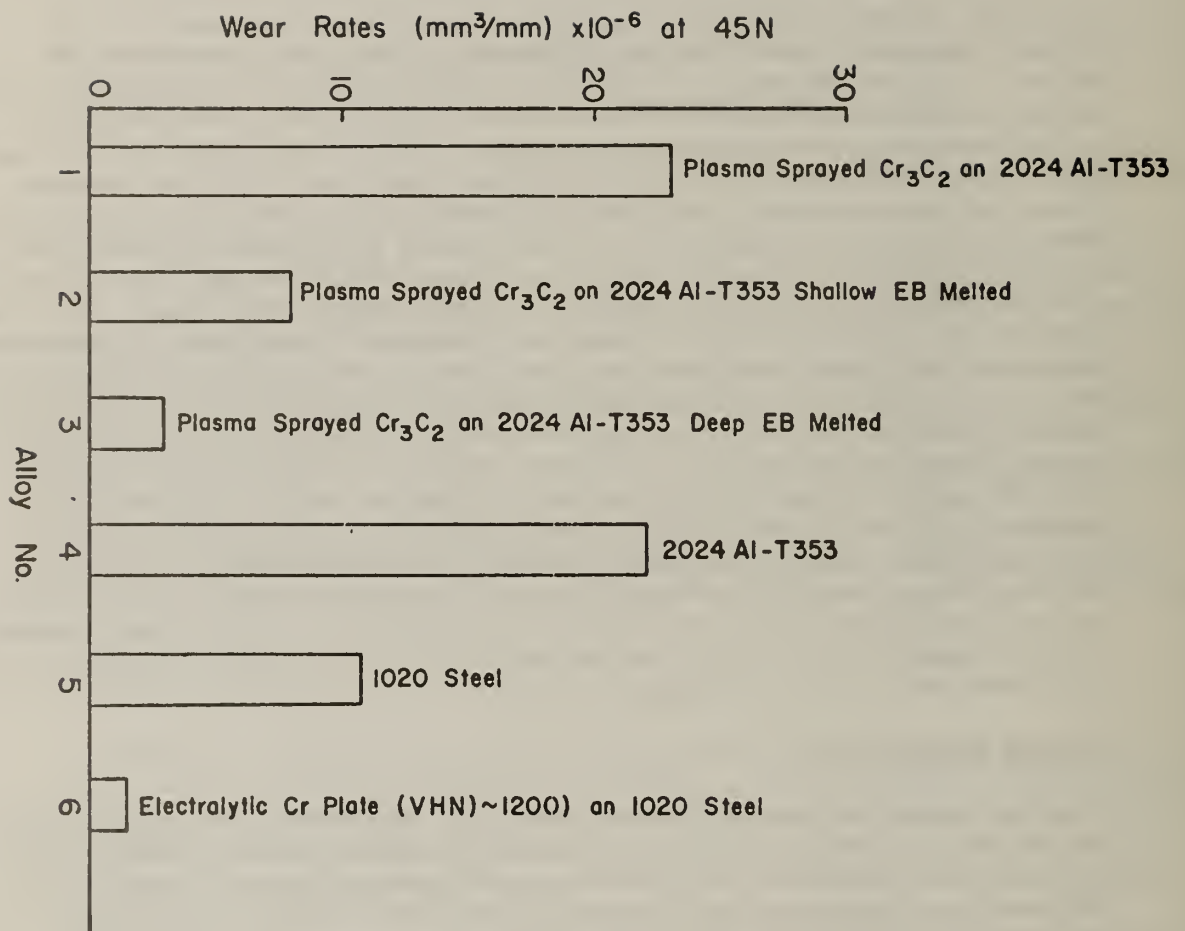


Figure 1 Abrasion wear rates for plasma sprayed and electron beam melted chromium carbide coatings on 2024 aluminum.



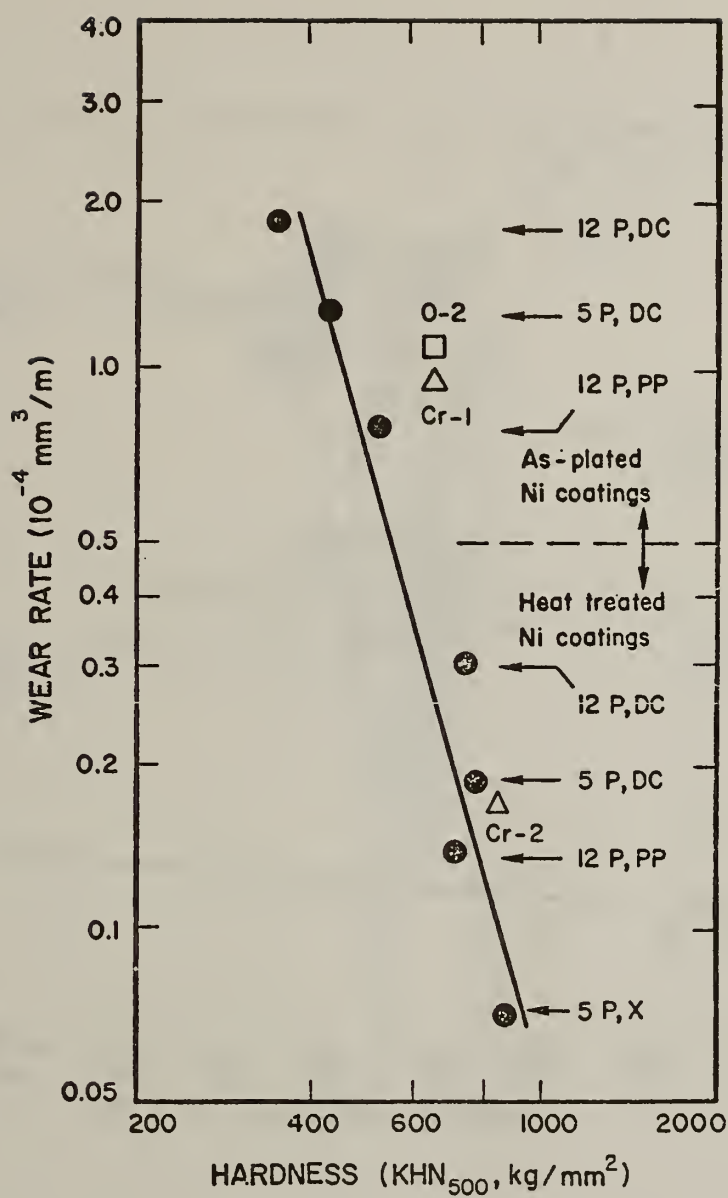


Figure 2 Dry sliding wear rates for various nickel-phosphorus alloy coatings on tool steel vs microhardness.

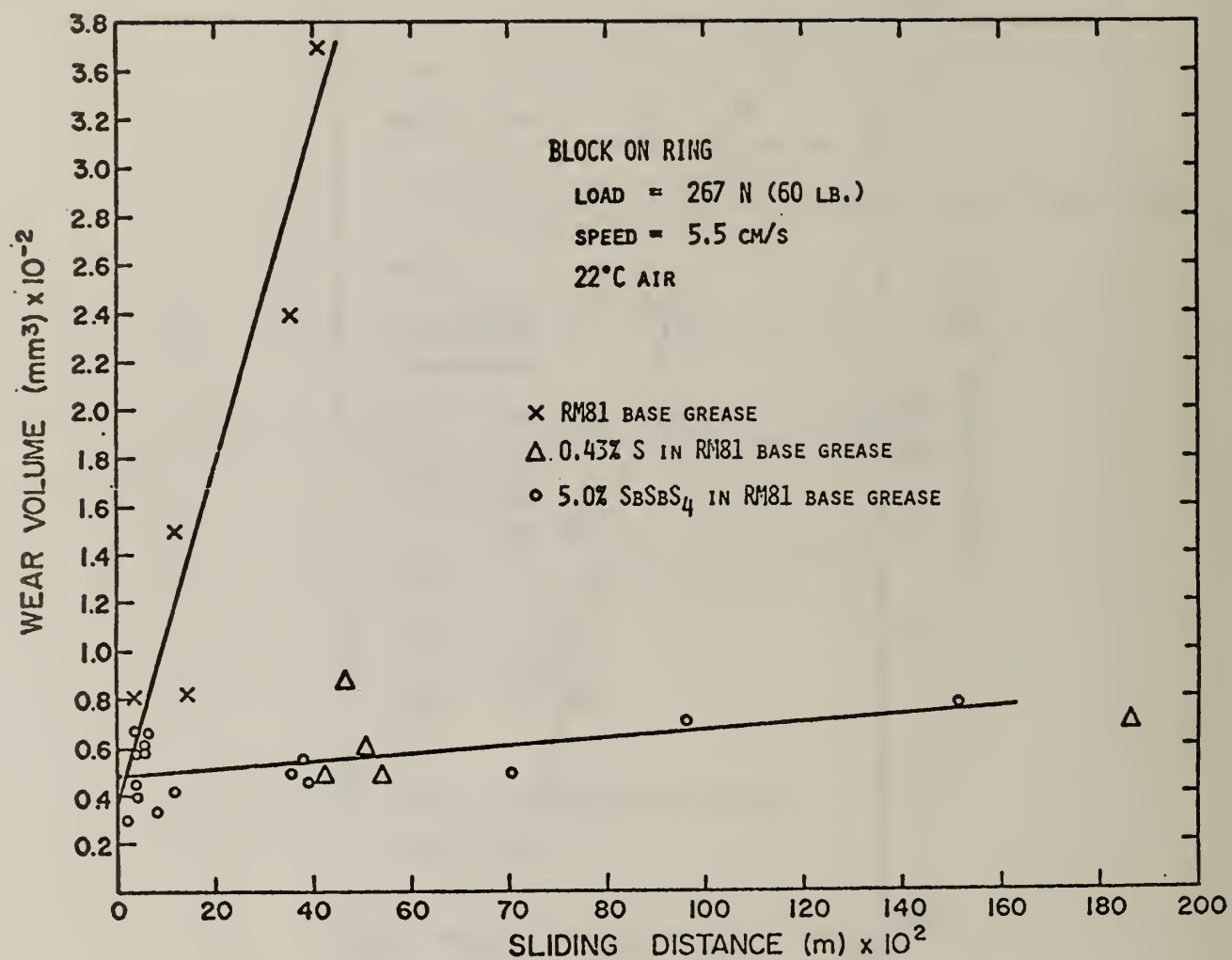


Figure 3 Wear volume vs sliding distance for SbSbS<sub>4</sub> and other lubricants on steel.

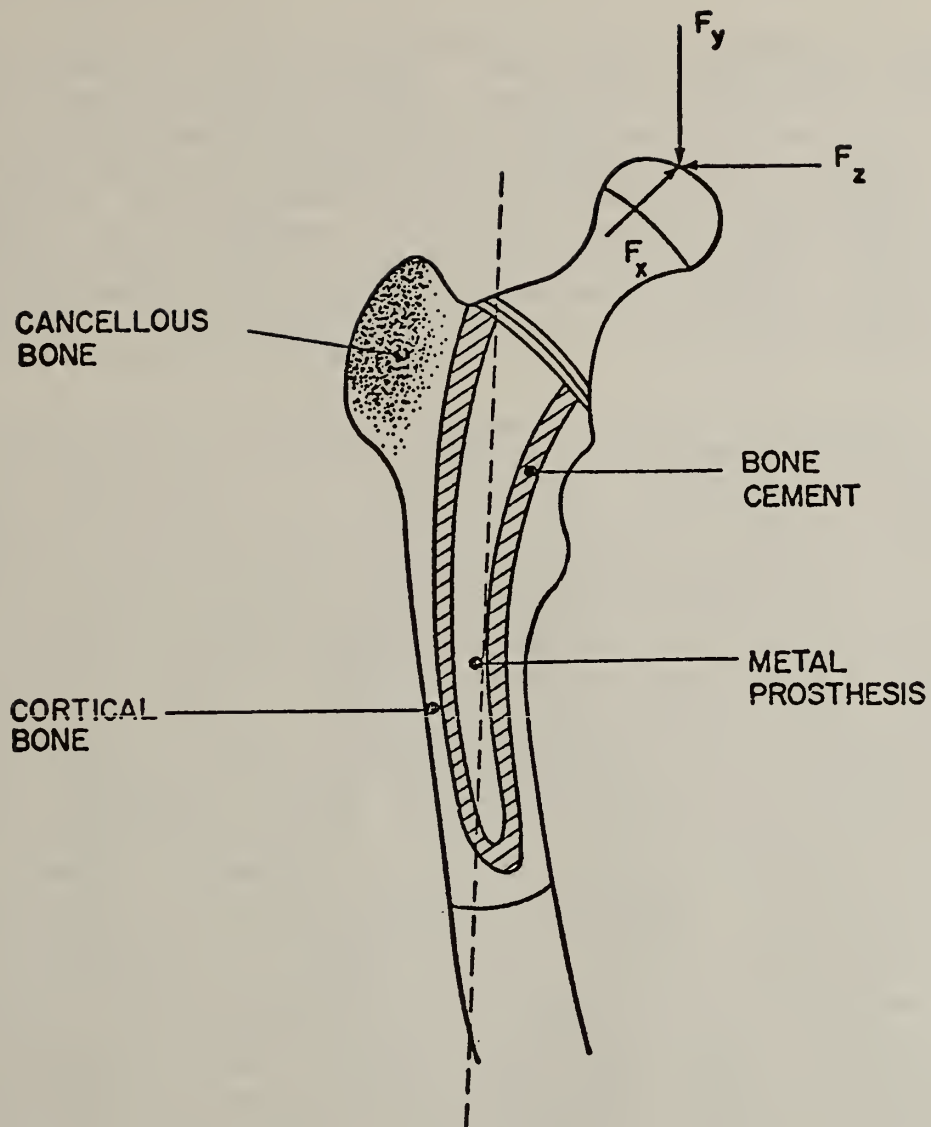


Figure 4 Total hip replacement prosthesis and applied joint force components.





CHEMICAL METALLURGY  
Task 12145

The interplay between thermodynamic predictive models and the formation and stability of alloy phases is the central theme of this task's activities. This theme is developed in data, theory, and experiment. Conventional and new experimental techniques are combined with theoretical models in the determination and prediction of phase diagrams. Special emphasis is placed on the development of on-line computer graphic systems. In addition to its fundamental scientific interest, advancement in the understanding of phase diagrams is essential to permit greater flexibility in development of new alloys for improved performance, ease of processing, reduced cost, and energy use, as well as in providing substitutes for scarce elemental additions.

The joint effort mandated by agreement between the Directors of the National Bureau of Standards (NBS) and the American Society of Metals (ASM) has continued to provide critically evaluated phase diagram and other constitution data as well as related bibliographic material. Technical oversight of this program and work on selected systems is being carried out by the Alloy Data Center (supported in part under this task and by the Office of Standard Reference Data (OSRD)). ASM continues to support a Research Associate at NBS for this project and has initiated a four million dollar fund raising effort from industry. A quarterly, Bulletin of Alloy Phase Diagrams, is also published under this program. The scope of the major effort initiated last year to evaluate binary phase diagrams at NBS, has been greatly extended to include iron-based and aluminum-based systems in addition to previously initiated evaluations of titanium-based systems. Thus, all binary alloy phase diagrams based on elements of commercial and national interest like Fe, Al, and Ti are evaluated at the National Bureau of Standards. The projects of compiling and evaluating phase diagram data for all binary titanium, aluminum and iron-based alloys have three aspects: (1) to provide accurate phase stability data compilations; (2) to serve as a model for the rest of the categories in the NBS/ASM joint program on binary phase diagrams; and (3) to create a modern computer-based phase stability data compilation. The program has four basic and interrelated components. These include compilation and evaluation, development of bibliographic methods, thermodynamic optimization, and development of computer software.

Experimental phase diagram work has been concerned with the binary and ternary systems relevant to the Ti and Al rich corner of the quinary system Ti-Al-Mo-Nb-Ta. This work is being done with the partial support from the Office of Naval Research (ONR). The Ti alloys involved in this system have important present and potential practical advantages. Their high corrosion resistance makes them attractive for marine and chemical processing applications, and their high strength to weight ratio makes them valuable in aviation and space technology.

Other activities in this task include theoretical work on understanding parameters important to alloy phase stability, and a major effort in the evaluation of possible nonuniformities in two aluminum alloys used by the National Aeronautics and Space Administration in the Space Shuttle.

The latter program, while reported under this task, has involved many of the scientists in the other groups in the Metallurgy Division.

#### Alloy Phase Stability Subtask 1 of Task 12145

K. J. Bhansali, L. H. Bennett, J. R. Cuthill, D. J. Kahan, A. McAlister, J. L. Murray, M. E. Read, L. J. Swartzendruber, and R. D. Shull

We are pursuing a program of three interconnected parts: critical evaluation and compilation of binary phase diagram data, experimental work on phase stability on alloy systems selected with a view to complementing the evaluation program, and the theory of phase stability, stressing the prediction of the heat of formation of transition metal binary alloys.

#### Alloy Phase Diagram Data Center Activities

All activities revolve about a collaborative alloy phase diagram critical evaluation program with the American Society for Metals. At NBS the scope of the phase diagram program has been greatly extended, to include not only the Ti category, but also the important categories of Al and Fe binary systems. Archie McAlister and Joanne Murray are the joint category editors for Al, Lydon Swartzendruber is the category editor for Fe, and Joanne Murray is the category editor for Ti. This program is active in the preparation and dissemination of a comprehensive computer-accessible data base of binary and multicomponent alloy phase stability data. The data which are to become accessible by computer include not only the graphical phase diagrams themselves, but relevant metastable equilibria and thermodynamic properties, an annotated bibliographic data base, and the text of the evaluation. In order to carry out the critical evaluation of data, an International Council of experts in thermodynamics and phase stability acts as advisors on the scope and format of the evaluations, supported by additional panels of experts dealing separately with binary and multi-component systems. The actual evaluation of the phase diagram data is being carried out throughout the world at institutions with special expertise in certain alloy systems. In addition to evaluations being done at NBS, evaluations are in progress in the categories: actinides, alkali metals, rare earths, Be, Cu, V, Zn and Cd, Nb, Zr, Mo, Mg, Co, Cr, hydrides, Ni, Si and Ge, and platinum metals.

The first seven issues of the Bulletin of Alloy Phase Diagrams have been published. This Bulletin, edited at NBS and published by ASM, is the main method of rapid dissemination of evaluated phase diagrams produced by category editors. The Bulletin also has acted as a vehicle for open review, and comments from the readers are published. New evaluations are being published from the Ti, Al, V, Zr, and Cu categories.

Evaluations of binary systems of Ti with all the transition metals through the Ni-column have been completed. In the Al-category Al-Mg, -Zn, -Be, and -Li have been completed and -Cd, -Ga, -In, and -Cu are in progress. In the Fe category, pure Fe and Fe-Ru are in progress. This work is serving to define the scope and organization of phase stability data, to provide a role for thermodynamic modeling in both the evaluation of data and the creation of accurate graphical diagrams. It also has



stimulated the development of the computer tools required for the establishment of a computer data base organized on sound metallurgical principles. An expansion of the evaluation program to ternary systems is planned to begin within the next year.

NBS has available computer programs for the calculations and optimization of phase diagrams from thermodynamic data, and for the on-line graphical display of phase diagram data input either from a calculation or directly at the terminal. A new version of the thermodynamic program has been obtained which will allow us to use the more sophisticated quasi-chemical and sublattice models; also Dr. Bo Sundman of the Royal Institute of Technology, Stockholm, has agreed to provide NBS with his program to optimize multisublattice free energy functions. Progress has been made this year in representing both thermochemical and graphical phase diagram data in a computer file structure suitable for use in a database. Use has been made of a "list structure" which is program independent, freely formatted, easily edited, and equally interpretable by human users and computer programs.

We are advising ASM in the preparation of an on-line phase stability bibliography. John Cuthill is an ASM Research Associate working on this data base to be set up at Bibliographic Retrieval Service (BRS). Progress has been made in the development of formats for the annotation of phase diagram papers and the dissemination of formats to category editors. Uniform annotations of the phase diagram literature will allow complete bibliographies to be retrieved for both broad and limited topics in phase equilibria.

#### Experimental Phase Diagram Program

Experimental phase diagram concerned with the binary and ternary systems relevant to the Ti and Al rich corner of the quinary system Ti-Al-Mo-Nb-Ta. This work is being done with partial financial support from the Navy. The Ti alloys involved in this system have important present and potentially practical advantages. Their high corrosion resistance makes them attractive for marine and chemical processing applications and their high strength-to-weight ratio makes them valuable in aviation and space technology. With better understanding of Ti phase diagrams, it may be possible to reduce titanium processing costs so that titanium alloys could substitute for some stainless steels, as a means of reducing the U.S. dependence on imported chromium. Increased knowledge of Ti alloy phase formation can provide means of improving weldability.

Experimental work on these Ti-Al systems at NBS has been designed to overcome the experimental difficulties which have resulted in conflicting reports of several Ti diagrams in the literature. Contamination easily occurs in long anneals; principally oxygen cannot be removed, and the presence of aluminum may make hydrogen removal difficult as well. Special attention has been given to the production of pure samples; the oxygen content of samples now being prepared is less than 250 ppm, very low for Ti alloys. With carefully prepared samples, we have investigated selected regions of the phase boundaries using transverse-electromagnetic (TEM), optical metallography, and differential scanning calorimetry (DSC). Professor R. C. Reno, who is visiting NBS from the University of Maryland, has made the TEM measurements for these studies. In addition,

the order/disorder transition in the binary Ti-Al system has been studied using magnetic susceptibility measurements.

The phases being investigated are the bcc solid solution ( $\beta$ ), the disordered hexagonal-close-packed (hcp) solid solution ( $\alpha$ ), and the ordered hcp phase ( $\alpha'$ ). After precision determinations of the  $\beta/\alpha$  and  $\alpha/\alpha'$  boundaries had been made in the binary Ti-Al system, the effect of 0.25 and 0.50 at. % Mo on the  $\alpha/(\alpha + \beta)$  and  $\alpha/\alpha + \alpha'$  boundaries was monitored; thus the Ti-Al edge of the ternary Ti-Al-Mo diagram is mapped. For the first time the order/disorder transition  $\alpha/\alpha'$  has been monitored using DSC, and the  $\alpha/\alpha'$  transition has been shown to be relevant for the study of the Ti-6211 alloy.

A Differential Scanning Calorimeter was obtained from Mettler Corporation for use in detection of solid state phase transformations. It is presently being modified and calibrated so that this apparatus may be used as a quantitative tool for determining precise transformation temperatures and for determining heats of transformation. Use of this tool is presently being made to determine the Ti-Al and the Ti-rich end of the Ti-Al-Mo phase diagrams.

Other experiments of fundamental significance to phase stability are underway. Metallic glasses and metastable crystalline compounds are one class of material of great interest. They have often been found to possess more desirable properties (e.g., corrosion resistance, strength, hardness, and ductility) than their equilibrium counterparts. In pursuit of this interest, a vacuum melt spinner has been constructed in which the molten alloy is solidified very quickly by impinging the liquid onto a copper wheel rotating at a speed of 10,000 rpm. For a glass produced in a 77 Pd-6 Cu-17 Si alloy, Dr. Moshe Rosen, a visitor to NBS from The Johns Hopkins University, has succeeded in monitoring its crystallization by ultrasound velocity measurements.

In conjunction with David Lashmore of the Materials Chemistry Division, studies of pulsed electrodeposited amorphous nickel-phosphorus alloys containing up to 42 at. % phosphorus have been carried out. It was shown, using nuclear magnetic resonance techniques, that these metallic glasses exhibit polymorphism, in addition to any continuous structural relaxation.

#### Fundamental Theory

In collaboration with Dr. R. E. Watson of Brookhaven National Laboratory, further advances have been made in the understanding of the quantum mechanical basis of alloy phase stability. A new correlation has been discovered for transition-metal alloys, in analogy with the well-known Hume-Rothery relative valency rule for nontransition-metal alloys. The relative solid solubility of two transition metals in each other has been shown to be related to the relative proximity of the components to a half-filled d band. Explanations based on Friedel band theory and on Engel-Brewer electron configuration theory have been advanced.

A new understanding of volume effects in transition-metal alloying has been provided. The relatively modest volume contractions (or expansions)



occurring on alloying does not correlate well with the heats of formation, but a useful correlation has been obtained that relates these volume effects to electronegativity trends. The correlation holds so well for the bulk of the transition and noble metal alloy systems that it can be employed to estimate volume effects for cases where they have not been observed. This should prove of use in calculating enthalpies of alloy formation.

A new study has been initiated to extend the Turnbull rule for volume effects in transition-metal-metalloid amorphous and crystalline alloys.

Nondestructive Evaluation of Nonuniformities in 2024 Aluminum Alloy Plate--  
Relationship to Processing.

Subtask 2 of Task 12145

L. K. Ives, L. J. Swartzendruber, W. J. Boettinger, M. Rosen, S. D. Ridder, F. S. Biancaniello, R. C. Reno, D. B. Ballard, and R. Mehrabian

Nondestructive evaluation (NDE) using eddy-current conductivity and hardness measurements form an essential part of the quality control of aluminum alloy plates used for aerospace vehicles. The relationship between the NDE measurements and the important mechanical properties are affected by a large number of variables including: chemical composition; cast structure; ingot scalping; solution heat treatment and quenching; mechanical working; and aging treatment. At the request of the National Aeronautics and Space Administration, a number of these relationships have been explored for 2024 aluminum alloy. This work is a continuation of our previous efforts on 2219 aluminum alloy and is motivated by a concern that improperly treated plates with "soft spots" may have been incorporated into structures on the Space Shuttle. A major result of our research has been a delineation of which alloy tempers and plate thicknesses are most likely to contain soft spots due to specific processing errors known to have occurred in a large number of plates.

The present studies include the following:

- (1) Studies on as-received material. This includes a 15 cm (6 in.) plate of 2024-T851, an 0.635 cm (1/4 in.) thick plate of 2024-F, and a direct chill cast ingot of 2024, all obtained from the Reynolds McCook plant.
- (2) Investigation of the phases and inclusions present in cast 2024 aluminum alloy with the aim of determining the degree of micro- and macrosegregation and identifying the inclusions present in the as-cast ingots.
- (3) Determination of a set of C-curves which can predict the mechanical and NDE properties for any type of quench following the solution heat treatment. Two tempers, T851 and T351, were investigated.
- (4) Transmission electron microscope studies of the stable and metastable phases present an attempt to relate the observed microstructural changes to the measured changes in mechanical and NDE properties.



- (5) A study of the ultrasonic wave propagation as a function of thermo-mechanical treatment of the alloy with the objective of establishing a correlation between ultrasonic data and mechanical properties and of providing an additional NDE parameter to better characterize the material.
- (6) A nondestructive evaluation of the age hardening sequence by means of dynamic eddy-current conductivity measurements.
- (7) Use of a heat flow model to calculate almost all conceivable heat flow conditions anticipated during the quench of 2024 aluminum alloy plate from the solution heat treatment temperature of 495 °C. The calculated time-temperature data were then coupled to the C-curves, and the variations in properties across different thickness plates for the worst and best heat flow conditions were predicted.

Predictable macrosegregation was obtained in laboratory ingots of 2024 aluminum alloy. It was found that macrosegregation of copper and other alloying additions in direct chill cast ingots of 2024 aluminum alloy cannot be completely eliminated by chill face scalping and subsequent thermomechanical treatment. Although good scalping practice should maintain compositions within specified limits with no deterioration in mechanical properties, the macrosegregation remaining in the finished plate product will contribute to the scatter observed in the NDE measurements. Further, because of the large copper content, variations near the chill face, surface hardness, and eddy current measurements are necessarily very sensitive to scalping depth in their ability to evaluate the condition of finished alloy plate.

A large number of samples were taken from a 0.635 cm thick plate of 2024 aluminum alloy in the F temper and processed to the T851, T351, or T4 temper. During processing to these tempers the quench following solution heat treatment was varied, giving a series of samples with a wide range of microstructures and hence mechanical properties. A schematic of the thermomechanical treatments is shown in figure 1. As shown in this figure, two types of "pre-aging" treatment, labeled sequence A and sequence B, were used. The hardness, eddy-current conductivity, yield strength, ultimate tensile strength, elongation, and area reduction of these samples were measured. The data accumulated were used to construct a set of approximate C-curves from which the alloy properties can be determined for any time-temperature cycle of the quench following solution heat treatment. The C-curves can also be used to generate correlations between mechanical and NDE properties. An example is shown in figure 2. The C-curves were also combined with time-temperature data from a computerized heat flow model to predict the variations in properties across plates of different thicknesses for both sequence A and sequence B type pre-aging heat treatments. It was found that the T851 temper is quite "quench sensitive" in the sense that the ultimate tensile strength falls below specification for the "worst possible quench" case for very thin plates.

TEM studies were carried out on a large number of specimens in an 120 kV instrument equipped to operate in the scanning transmission (STEM) mode as well as in the conventional transmission mode. The instrument was

also equipped with an x-ray energy dispersive spectrometer which permits the determination of elemental composition on a microscopic size scale. A major objective was to identify those microstructural changes that were responsible for the mechanical and physical properties delineated in the C-curve representations. Although the microstructure as a function of pre-aging is complex, it appears that pre-aging induced precipitates can contribute to the strength and are subject to overaging during further heat treatment. This provides a mechanism for the loss of strength which can account for the fact that the strength of the T851 temper is actually reduced below that of the T351 temper given the same pre-aging heat treatment (rather than being raised as occurs for properly quenched material).

The objective of the ultrasonic studies was to determine the extent to which a correlation exists between the mechanical and ultrasonic properties. For this purpose, the absolute, rather than the relative, values of the sound velocity and ultrasonic attenuation are required. The data have to be determined, consistently, to a high degree of accuracy so as to enable a comparison to be made between specimens of unknown thermal history, and to correlate these data with the ultimate mechanical properties of the material. The absolute values of sound velocity and ultrasonic attenuation were determined to within  $\pm 1 \text{ ms}^{-1}$  and  $\pm 0.02 \text{ dB}$ , respectively. The extent to which ultrasonic attenuation correlates with hardness is illustrated in figure 3. The behavior of the ultrasonic attenuation is correlated with the behavior of the hardness, i.e., softer material has higher attenuation values. The higher attenuation values of the B sequence, relative to the A sequence can be explained by a difference in microstructure between the two sequences. These results, along with the other results mentioned above, have been incorporated into a final report.

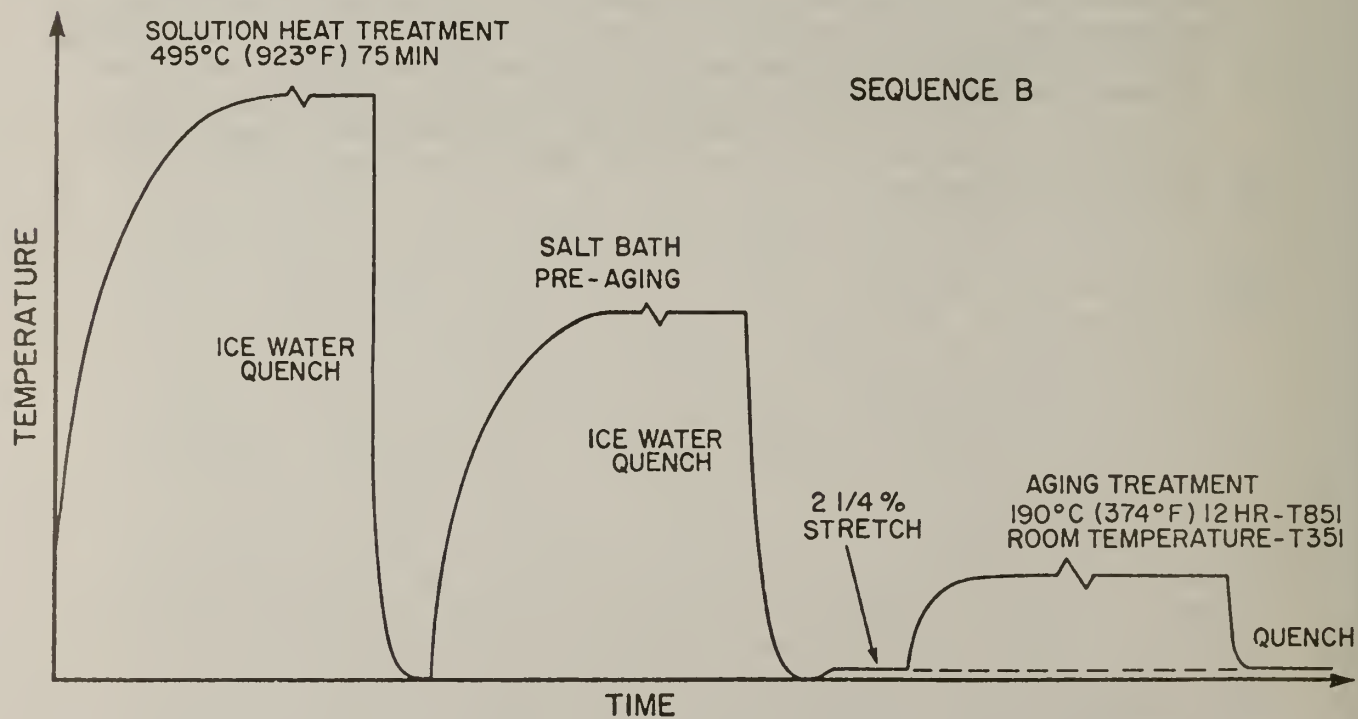
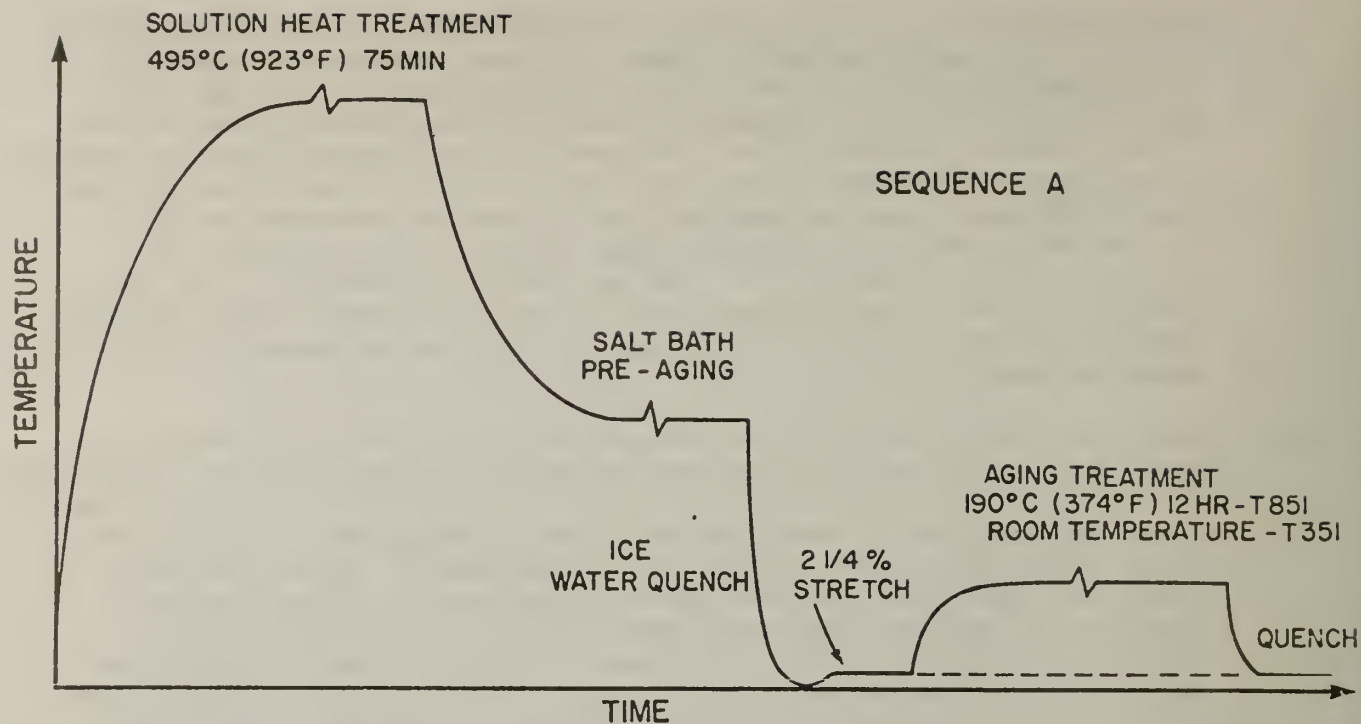


Figure 1 Schematic representation of the thermomechanical treatment sequences given the 2024-T851 and 2024-T351 aluminum alloys.



# ULTIMATE TENSILE STRENGTH VS CONDUCTIVITY 2024-T851

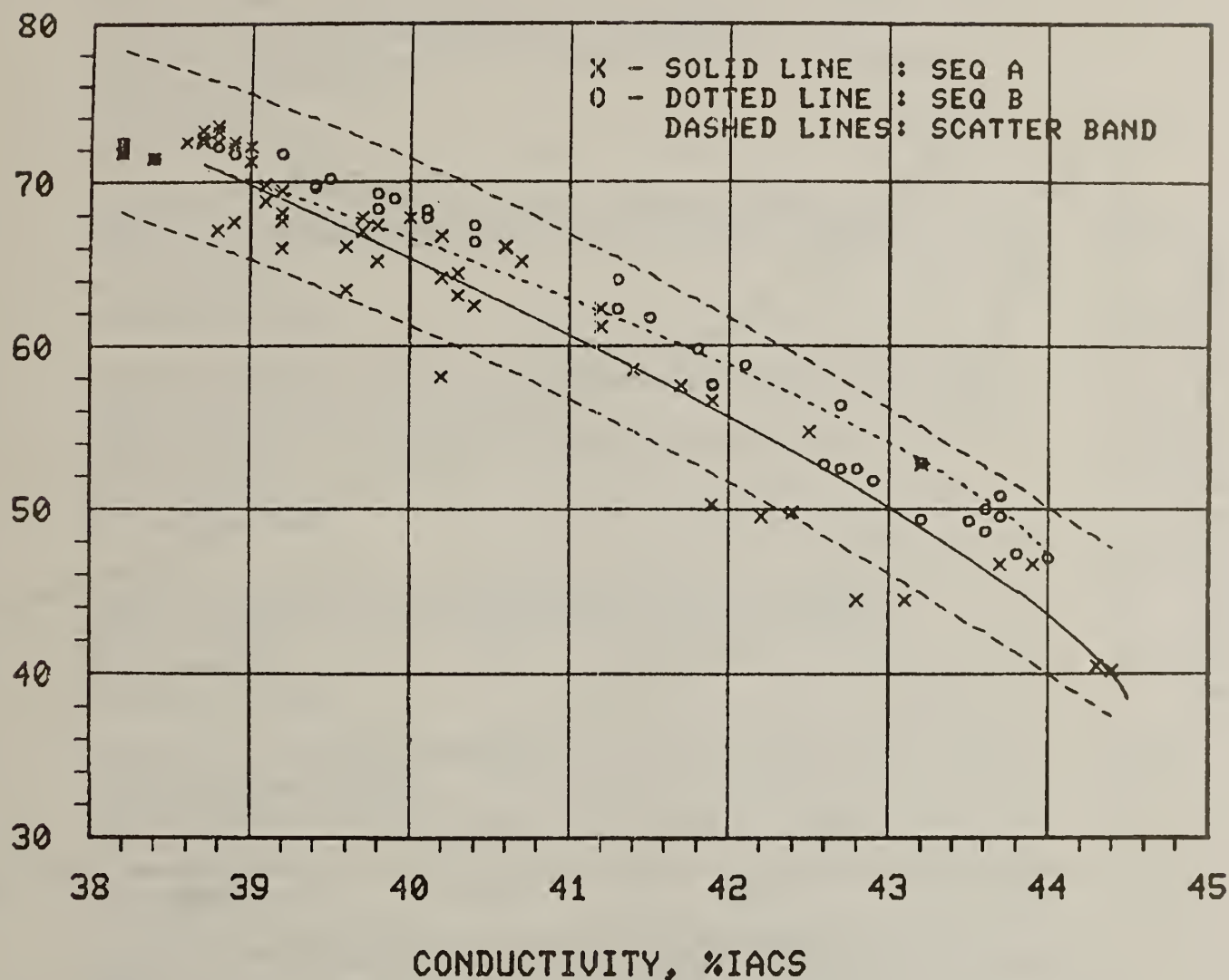


Figure 2 Comparison of ultimate tensile strength vs conductivity data for 2024-T851 with the correlations predicted by the C-curves. The dashed lines are the scatter band (~ 95 percent confidence level) obtained from a least squares quadratic fit to the data.

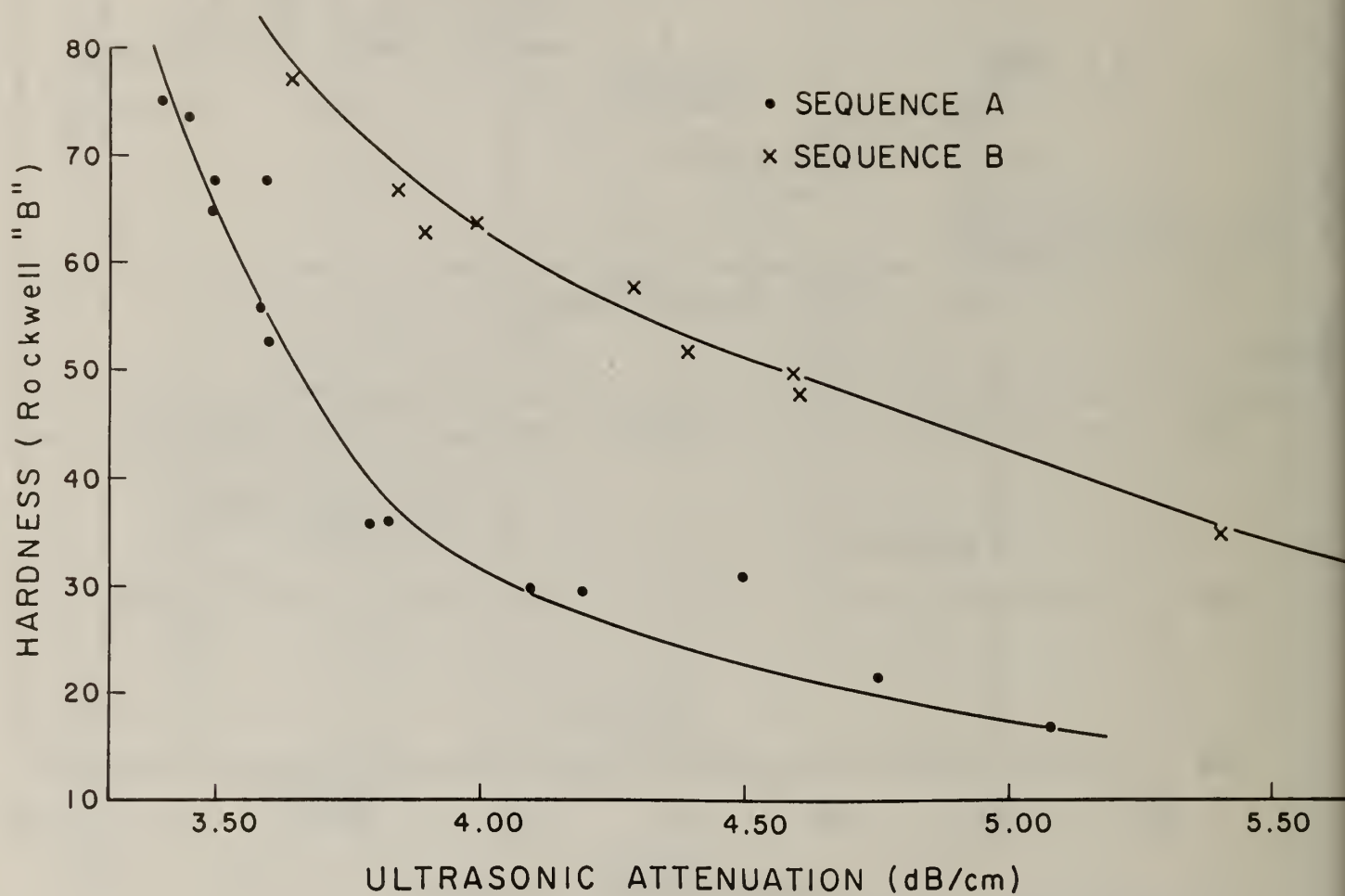


Figure 3 Variation of the ultrasonic attenuation as a function of hardness in 2024 aluminum alloy pre-aged by sequences A and B prior to aging.

Other Activities of the  
Metallurgy Division

Invited Talks

Science-Career Opportunities for both Graduate and Undergraduate  
Students at the National Bureau of Standards

Science Faculty, University of Puerto Rico, Rio Piedras and  
Mayaguez, Puerto Rico

G. J. Mattamal

September 14, 1981

Electrocatalysis on WC and Related Compounds and Alloys

1981 Fall Meeting of the Metallurgical Society of AIME,  
Louisville, KY

A. J. McAlister

October 12, 1981

A Relative Valency Rule for Terminal Solubilities of Transition  
Metal-Transition Metal Alloys

1981 Fall Meeting of the Metallurgical Society of AIME,  
Louisville, KY

D. A. Goodman

October 13, 1981

Diffusion Driving Forces Produced by Defect Fluxes

1981 Fall Meeting of the Metallurgical Society of AIME,  
Louisville, KY

J. R. Manning

October 13, 1981

The Role of Convection on Solute Segregation During Alloy Solidi-  
fication in Microgravity

1981 Fall Meeting of the Metallurgical Society of AIME,  
Louisville, KY

S. R. Coriell

October 13, 1981

Gravitationally-Induced Convection During Unidirectional Solidification

1981 Fall Meeting of the Metallurgical Society of AIME,  
Louisville, KY

R. J. Schaefer

October 13, 1981

Wear Studies on Surface Melted Alloys

Oregon Graduate Center, Beaverton, OR

A. W. Ruff

October 14, 1981

The Bulletin of Alloy Phase Diagrams: A New Resource for the  
Metallurgical Community

1981 Fall Meeting of the Metallurgical Society of AIME,  
Louisville, KY

L. H. Bennett

October 14, 1981



Evaluation of Titanium Binary Phase Diagrams  
1981 Fall Meeting of the Metallurgical Society of AIME,  
Louisville, KY  
J. L. Murray  
October 14, 1981

Fundamental Aspects of Rapid Solidification  
David Taylor Naval Ship Research and Development Center,  
Annapolis, MD  
J. R. Manning  
October 22, 1981

Metallurgical Considerations in Wear  
Oregon Graduate Center, Beaverton, OR  
K. J. Bhansali  
October 23, 1981

Solidification at High Interface Velocities  
American Society for Metals, Oak Ridge, TN  
R. Mehrabian  
October 29, 1981

Wear Studies on Coated and Surface Melted Alloys  
Lehigh University, Bethlehem, PA  
A. W. Ruff  
November 3, 1981

Real Time Topography with X-Ray Image Magnification  
1981 Annual Meeting of the Materials Research Society, Boston, MA  
M. Kuriyama  
November 16, 1981

Growth Kinetic Limitations During Rapid Solidification  
1981 Annual Meeting of the Materials Research Society, Boston, MA  
W. J. Boettinger  
November 17, 1981

Morphological Stability of Electron Beam Melted Aluminum Alloys  
1981 Annual Meeting of the Materials Research Society, Boston, MA  
R. J. Schaefer  
November 17, 1981

Convective and Interfacial Instabilities During Solidification of  
Succinonitrile Containing Ethanol  
1981 Annual Meeting of the Materials Research Society, Boston, MA  
R. J. Schaefer  
November 19, 1981

Studies of Liquid Metal Surface Using Auger Spectroscopy  
1981 Annual Meeting of the Materials Research Society, Boston, MA  
S. C. Hardy  
November 19, 1981

Dry Sliding Wear Studies of NiP and Cr Coatings on 0-2 Tool Steel  
ASTM Committee G-2, Phoenix, AZ  
A. W. Ruff  
December 9, 1981

Microstructures and Fatigue of Implant Alloys  
Johns Hopkins University, Baltimore, MD  
A. C. Fraker  
February 2, 1982

Metallurgical and Corrosion Research at NBS  
Indian Institute of Technology, New Delhi, India  
K. J. Bhansali  
February 3, 1982

Metallurgical and Corrosion Research at NBS  
Indian Institute of Science, Bangalore, India  
K. J. Bhansali  
February 9, 1982

Metallurgical Considerations in Wear  
Indian Institute of Technology, Bombay, India  
K. J. Bhansali  
February 19, 1982

In Vitro Corrosion Studies of Implant Metals  
Washington Bioengineering Group, Bethesda, MD  
A. C. Van Orden  
March 30, 1982

Growth Kinetic Limitations in Rapid Solidification  
Harvard University, Cambridge, MA  
W. J. Boettinger  
April 8, 1982

Wear Tests to Characterize Recycled Oil  
The American Society of Lubrication Engineers, Chicago, IL  
L. K. Ives  
April 15, 1982

Monitoring the Sliding Contact Conditions in Laboratory Wear Tests  
of Metals Using Time-Dependent Variations in Friction Coefficients  
Thirty-Fifth Mechanical Failures Prevention Group Symposium,  
Gaithersburg, MD  
P. J. Blau  
April 21, 1982

Morphological Stability  
Harvard University, Cambridge, MA  
S. R. Coriell  
April 22, 1982

Nickel (11) Ion Interactions with Human Serum Albumin  
Eighth Annual Biomaterials Meeting, Orlando, FL  
G. J. Mattamal  
April 26, 1982

The Influence of Small Variations in Composition on the Corrosion  
of Cobalt-Chromium Alloys  
The Society for Biomaterials, Orlando, FL  
A. C. Van Orden  
April 27, 1982

Wear Studies on Coated and Surface Melted Alloys  
Johns Hopkins University, Baltimore, MD  
A. W. Ruff  
April 28, 1982

Diffusion-Induced Grain Boundary Migration  
The American Ceramic Society, Cincinnati, OH  
D. B. Butrymowicz  
May 3, 1982

Convective and Interfacial Instability During Unidirectional Upward  
Solidification of Succinonitrile  
The American Ceramic Society, Cincinnati, OH  
R. J. Schaefer  
May 4, 1982

The Bulletin of Alloy Phase Diagrams and CALPHAD a Community Interest  
CALPHAD XI, Argonne National Laboratory, Chicago, IL  
L. H. Bennett  
May 16, 1982

Relative Terminal Solubilities of Transition Metal-Transition Metal  
Alloy System  
CALPHAD XI, Argonne National Laboratory, Chicago, IL  
L. H. Bennett  
May 17, 1982

Evaluation and Calculation of the Al-Zn System  
CALPHAD XI, Argonne National Laboratory, Chicago, IL  
J. L. Murray  
May 19, 1982

Wear Considerations for Coatings  
Surtech and Surface Coating Exposition  
ASM and Chemical Coaters Association, City, ST  
K. J. Bhansali  
May 19, 1982

Applications of New Ideas in Artificial Intelligence to the Inter-  
rogation of Phase Diagram Database  
CALPHAD XI, Argonne National Laboratory, Chicago, IL  
J. L. Murray  
May 20, 1982



An X-Ray Method for Quantitative Analysis of Hardness Indentations  
in Crystals  
Microhardness-Related Research Seminar, Gaithersburg, MD  
M. Kuriyama  
May 25, 1982

Some Unconventional Applications of the Knoop Test Method for Micro-  
structural Analysis  
Symposium on Microhardness-Related Research, Gaithersburg, MD  
P. J. Blau  
May 25, 1982

Morphological and Convective Instabilities During Solidification  
Twenty-Fourth COSPAR Meeting, Ottawa, Canada  
S. R. Coriell  
May 26, 1982

Effect of Test Parameters on Wear Rate  
ASTM G-2 Workshop Symposium, St. Louis, MO  
L. K. Ives  
June 9, 1982

Metallurgical Factors Affecting Galling Wear  
Gordon Research Conference on Friction, Lubrication and Wear,  
New London, NH  
K. J. Bhansali  
June 15, 1982

Wear Microstructures  
Gordon Research Conference on Friction, Lubrication and Wear,  
New London, NH  
L. K. Ives  
June 15, 1982

Applications of Synchrotron Radiation to Materials Science  
Materials Research Council Meeting, LaJolla, CA  
M. Kuriyama  
July 6, 1982

On the Geometry of Zeroed Polynomials of High Degree  
SIAM Meeting, LaJolla, CA  
J. A. Simmons  
July 18, 1982

Structure of Passive Films on Iron  
Intl. Conf. on Electronic and Molecular Structure of Electrode  
Electrolyte Interfaces, Logan, UT  
G. G. Long  
July 25, 1982

Surface Tension of Liquid Metals at Elevated Temperatures  
Gordon Research Conference, Meriden, NH  
S. C. Hardy  
July 28, 1982

Science Career Opportunities for Gifted Students at the National  
Bureau of Standards  
American University, Washington, DC  
G. J. Mattamal  
August 13, 1982

The Influence of Chemical Factors on Alloy Phase Diagrams--Modern  
Hume-Rothery Parameters  
Alloy Development Workshop, Los Alamos National Laboratory,  
Los Alamos, NM  
L. H. Bennett  
September 8, 1982

Evaluations of Alloy Phase Diagrams--Experimental Data and Thermo-  
dynamic Models  
Alloy Development Workshop, Los Alamos National Laboratory,  
Los Alamos, NM  
L. H. Bennett  
September 9, 1982

#### Division Seminars

The Relationship Between Microstructure, Wear, and Debris  
Characteristics  
D. C. Furze  
Uxbridge, Middlesex, England  
October 13, 1981

Electron Metallography Study of Gas-Solid Reactions and Large Strain  
Deformation  
R. M. Fisher  
U.S. Steel Corporation, Monroeville, PA  
October 26, 1981

Weld Monitoring for Defects Using Acoustic Emission During Welding  
D. W. Prine  
GARD, Inc., Miles, IL  
October 30, 1981

Biomaterials and Biomechanics Related Failures of Total Hip Implants  
K. J. Bundy  
Johns Hopkins University, Baltimore, MD  
November 13, 1981

Ultra-High Resolution Chemical Analysis with the Atom Probe  
S. S. Brenner  
U.S. Steel Corporation, Monroeville, PA  
November 23, 1981

Welding Characteristics of Rare Earth and Low Sulfur Steels for Gas  
Pipelines  
H. Muir  
University of New South Wales, Sidney, Australia  
January 6, 1982

Biomaterials and Biomechanics Related Failures of Total Hip  
Prostheses

K. J. Bundy  
Johns Hopkins University, Baltimore, MD  
January 12, 1982

Ordering Reactions in Superalloys Based on the Nickel-Aluminum  
Molybdenum System

P. L. Martin  
Carnegie-Mellon University, Pittsburgh, PA  
March 31, 1982

Magnetic Properties and Applications of Amorphous Metallic Glasses

R. Hasegawa  
Allied Corporation, Morristown, NJ  
April 21, 1982

Abrasion Resistant Cast Composite Materials

P. Rohatgi  
Regional Research Laboratory for Bhopal, India  
May 6, 1982

Coarsening and Microsegregation During Nickel-Base Dendritic  
Crystal Growth

T. Z. Kattamis  
University of Connecticut, Storrs, CT  
May 6, 1982

Microstructure Characterization by in situ High Voltage Electron  
Microscopy and High Speed X-Ray Topography

T. Imura  
Nagoya University, Nagoya, Japan  
June 7, 1982

Creep and Diffusion in Metallic Glasses

F. Spaepen  
Harvard University, Cambridge, MA  
June 17, 1982

Tribology in West Germany

H. Czichos  
Bundesanstalt für Materialprüfung, Berlin-Dahlem, West Germany  
June 25, 1982

Acoustic Microscopy for Materials Studies

G. A. Briggs  
University of Oxford, Oxford, England  
July 2, 1982

A Statistical Interpretation of Erosion

D. Andrews  
University of Cambridge, Cambridge, England  
July 27, 1982



## Technical and Professional Committee Participation and Leadership

### American Association for Crystal Growth

S. R. Coriell and R. L. Parker, Executive Committee

### American Institute of Metallurgical Engineers

The Metallurgical Society

R. D. Shull, Member

Alloy Phases Committee of the Metallurgical Society

L. H. Bennett, Member, Past Chairman, and Liaison to ASM

Solidification Committee of the Metallurgical Society

W. J. Boettinger, S. R. Coriell, S. C. Hardy, J. R. Manning,

R. Mehrabian, S. D. Ridder, and R. J. Schaefer, Members

William Hume-Rothery Award Committee

L. H. Bennett, Member

### American Society of Lubrication Engineers

Wear Committee

K. J. Bhansali and L. K. Ives, Members

### American Society for Metals

P. J. Blau and A. C. Van Orden, Executive Committee,  
Washington, DC Chapter

A. C. Fraker, Executive Committee, Ex Officio,  
Washington, DC Chapter

Bulletin of Alloy Phase Diagrams

L. H. Bennett, Editor

D. J. Kahan and M. E. Read, Associate Editors

R. V. Drew, Editorial Assistant

Mass Transport Activity

J. R. Manning, Member

Phase Transformations Committee

R. Mehrabian, Member

Process Modeling Committee

J. R. Manning and R. Mehrabian, Members

American Society for Metals/American Institute of Metallurgical  
Engineers

Composite Committee

R. Mehrabian, Member

International Council for the ASM/NBS Program for Alloy Phase  
Diagrams

L. H. Bennett and R. Mehrabian, Members

American Society of Mechanical Engineers

Ad Hoc Working Group on Acoustic Emission, Section 5

J. A. Simmons, Member

Research Committee on Lubrication (Hardfacing and Coatings)

K. J. Bhansali, Member

American Society of Mechanical Engineers/American Society for Metals

Wear of Materials Conference Steering Committee

A. W. Ruff, Member and 1983 Vice-Chairman

American Society for Testing and Materials

A1: Steel, Stainless Steel, Related Alloys; Castings

R. L. Parker, Member

B2: Nonferrous Metals and Alloys

S. D. Ridder, Member

B5: Copper and Copper Alloys

M. E. Read and L. J. Swartzendruber, Members

B6: Die-Cast Metals and Alloys

R. Mehrabian, Chairman

B7: Light Metals and Alloys; Aluminum Alloy Ingots and Castings

W. J. Boettinger and R. D. Shull, Members

B9: Metal Powders and Metal Powder Products

J. R. Manning, Member

D32: Catalysts

A. J. McAlister, Member

E04: Metallography

D. B. Ballard, P. J. Blau, and L. J. Swartzendruber,  
Members

E04: Task Group on Microhardness Testing

P. J. Blau, Member

E04.03: Phase Diagrams Subcommittee

P. J. Blau, Member

E04.11.07: Metallography; Electron Metallography; Scanning  
Electron Microscopy

D. B. Ballard, Task Group Leader

E42: Surface Analysis

G. G. Long and A. J. McAlister, Members

E7: Nondestructive Testing  
L. H. Bennett and L. J. Swartzendruber, Members

E7.04: Acoustic Emission  
J. A. Simmons and R. B. Clough, Members

Joint Task Group on Acoustic Emission; System  
Calibration  
J. A. Simmons, Chairman

E9: Fatigue  
J. A. Simmons, Member

Task Group 3 - Residual Stress of Effect in Fatigue  
J. A. Simmons, Member

E9.03: Fatigue of Composite Materials  
J. A. Simmons, Member

F4: Medical and Surgical Materials and Devices  
A. C. Fraker and A. W. Ruff, Members

F4/G1: Joint Section on Corrosion of Implants  
A. C. Fraker, Co-Chairperson

G2: Erosion and Wear  
A. W. Ruff, Chairman  
K. J. Bhansali, P. J. Blau, and L. K. Ives, Members

G2.2: Solid Particle Erosion  
A. W. Ruff, Task Group Leader  
K. J. Bhansali, Member

G2.3: Wear  
K. J. Bhansali, P. J. Blau, L. K. Ives, and  
A. W. Ruff, Members

G2.91: Terminology and Definitions  
P. J. Blau, Chairman  
L. K. Ives, Member

Applied Mechanics Review  
R. B. Clough, Member, Review Staff

Florence Review Committee, Review of Scanning Electron Microscopes  
D. B. Ballard, Chairman

International Association for Dental Research  
G. J. Mattamal, Member

International Journal of Crystal Growth  
R. L. Parker, Deputy Principal Editor, Editorial Board



International Journal of Diffusion and Defect Data  
D. B. Butrymowicz, Advisory Board Member

Maryland Institute of Metals  
W. J. Boettinger, Executive Board Member

Materials Processing Center, Massachusetts Institute of Technology  
R. Mehrabian, Member Advisory Board

Materials Science and Engineering  
L. H. Bennett, Editor, Phase Diagram Section

Metallurgical Transactions  
L. H. Bennett and R. Mehrabian, Members, Board of Review

Visiting Committee, Department of Metallurgy and Materials Science  
Carnegie-Mellon University  
R. Mehrabian and R. L. Parker, Members

National Aeronautics and Space Administration, Space and Terrestrial  
Applications Steering Committee, Proposal Evaluation Advisory  
Subcommittee  
S. R. Coriell, Member

National Aeronautics and Space Administration, Materials Processing  
in Space Panel  
R. Mehrabian, Member

National Aeronautics and Space Administration, Universities Space  
Research Association  
R. Mehrabian, Member

National Materials Advisory Board, Committee on Superalloy Powder  
Alloys  
R. Mehrabian, Member

National Materials Advisory Board, Committee on Materials Substitu-  
tion Methodology  
R. Mehrabian, Liaison Member

National Materials Advisory Board, Committee on Rapid Solidification  
Processing  
R. Mehrabian, Chairman

National Science Foundation, Facilities Subcommittee of the  
Materials Research Advisory Board  
G. G. Long, Chairman

Society of Automotive Engineers/American Society of Testing and  
Materials Unified Numbering System for Metals and Alloys  
L. H. Bennett, NBS Representative

Society for Biomaterials Standards  
A. C. Fraker, Chairperson, Representative

Society for Experimental Stress Analysis  
Residual Stress Committee  
C. J. Bechtoldt and J. A. Simmons, Members

Society of Rheology  
R. Mehrabian, Member

US-USSR Technology Exchange Agreement  
Sub-Committee on Electro-Slag Remelting  
R. Mehrabian, Member

Welding Research Council, Committee on Hardfacing and Wear  
K. J. Bhansali, Member

### Publications

Boettinger, W. J. Conference on rapidly quenched metals. J. Metals 33: 21; 1981.

Boettinger, W. J.; Biancaniello, F. S.; Coriell, S. R. Met. Trans. 12A: 321; 1981.

Goodman, D.; Waterstrat, R. M. Comments of the Mn-Fe and Mn-Cr phase diagrams. Bull. Alloy Phase Diagrams 2: 299; 1981.

Yoo, K. C.; Roessler, B.; Armstrong, R. W.; Kuriyama, M. Scr. Metall. 15: 1245; 1981.

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Kuriyama, M.; Boettinger, W. J.; Cohen, G. G. Synchrotron radiation topography. Annu. Rev. Mater. Sci. 12: 23; 1982.

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Olson, C. D. SEM analysis of clad-ceramic coatings after hot corrosion testing. Bailey, G. W., ed. Proceedings of the 40th annual electron microscopy society of America meeting; 1982 August 9-13; Washington, DC. Claitor's Publ. 1982. p. 522.

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Schaefer, R. J.; Coriell, S. R. Materials processing in the reduced gravity environment of space, Guy E. Rindone, ed., Elsevier, 1982, p. 479.

Van Orden, A. C.; Chidester, J. L.; Fraker, A. C.; Sung, P. SEM studies of Co-Cr-Mo surgical implant alloy corrosion behavior. Bailey, G. W., ed. Proceedings of the 40th annual electron microscopy society of America meeting; 1982 August 16-19; Washington, DC. Claitor's Publ. 1982. p. 520.

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Bhansali, K. J.; Mehrabian, R. Abrasive wear of aluminum matrix composites. J. Metals; in press.

Blau, P. J. A comparison of micro-indentation hardness test methods using Cu, 52100 steel and an amorphous Pd-Cu-Si alloy. Metallography; in press.

Blau, P. J. Test of a rule of mixtures for dry sliding friction of 52100 steel on an Al-Si-Cu alloy. Wear; in press.

Blau, P. J. Monitoring the sliding contact conditions in laboratory wear tests of metals using time dependent-variations in friction coefficients. Early, J. G.; Shives, T. R.; Smith, J. H., eds. Proceedings of the 35th mechanical failures prevention group meeting; 1982 April 20-22; Gaithersburg, MD. Cambridge U. Pr.; in press.

Boettinger, W. J. Growth kinetic limitations during rapid solidification. Keart, B. H.; Giossen, B. C., eds. Chapter in Rapidly solidified amorphous and crystalline alloys; New York, NY: Elsevier North Holland; in press.

Butrymowicz, D.; Cahn, J.; Manning, J.; Newbury, D.; Piccone, T. Diffusion-induced grain boundary migration. Chapter in Grain boundaries and interfaces in ceramics, Vol. 15. Huer, A.; Yan, M., eds. New York, NY: Plenum Press; in press.

Chang, J.; Nadeau, R.; Rosen, M.; Mehrabian, R. Crystallization kinetics study of amorphous  $Zr_{50}Cu_{50}$  by means of ultrasonic measurements and microhardness. Scr. Metall.; in press.



Clough, R.; Wadley, H. Indentation loading studies of acoustic emission from temper and hydrogen embrittled A533B steel. Metall. Trans. A; in press.

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Kuriyama, M.; Cohen, G. X-ray extinction theory in the Bragg geometry. Z. Naturforsch. 37a: ; 1982; in press.

Long, G. G.; Kruger, J.; Black, D. R.; Kuriyama, M. Structure of passive films on iron using a new surface-EXAFS technique. Hansen, P. W. N., ed. Proceedings of the 1st international conference on electronic and molecular structure of electrode-electrolyte interfaces; 1982 July 25-30; Sagan, VT; in press.

Manning, J. R. Application of phase diagram information to alloy diffusion coatings. Bull. Alloy Phase Diagrams; in press.

Mattamal, G.; Kishore, K. Structure-viscosity relationship in some high molecular weight esters. J. Polym. Sci.; in press.

Murray, J. L. Calculations of stable and metastable equilibrium diagrams of the Ag-Cu and Cd-Zn systems. Metall. Trans. A; in press.

Oehl, C.; Swartzendruber, L. On the optimum applied field for magnetic particle inspection using direct current. Mater. Eval.; in press.

Parker, R. L. Ultrasonic measurement of solid/liquid interface position during solidification and melting of metals. Chapter in Applications of physics to the steel industry. Schwerer, F., ed. New York, NY: American Institute of Physics; in press.

Schaefer, R. J.; Coriell, S. R. Convective and interfacial instabilities during solidification of succinonitrile containing ethanol. Rindone, G. E., ed. Proceedings of the symposium on materials processing in the reduced gravity environment of space; 1981 November 16-19; Boston, MA. Elsevier North Holland; in press.

Schaefer, R. J.; Coriell, S. R.; Mehrabian, R.; Fenimore, C.; Biancaniello, F. Morphological stability of electron beam melted aluminum alloys. Kear, B. H., ed. Proceedings of the symposium on rapid solidified amorphous and crystalline alloys; 1981 November; Boston, MA; in press.

Wadley, H. N. G.; Simmons, J. A.; Stockton, C. K. Dynamic elastic displacements due to pulsed laser absorption at the surface of an infinite plate. J. Acoust. Soc. Am.; in press.

Watson, R. E.; Bennett, L. H. Volume effects in transition metal alloying. Acta Metall.; in press.

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### Special Reports

Mehrabian, R.; Persh, J. Report on the first workshop on rapid solidification technology. Nat. Bur. Stand. (U.S.) NBSIR 81-2439; 1982. 52 p.

Ives, L. K.; Peterson, M.; Harris, J. S.; Boyer, P. A.; Ruff, A. W. Investigation of the lubrication mechanisms of the complex metal sulfide,  $\text{SbSbS}_4$ . Nat. Bur. Stand. (U.S.) NBSIR 82-2545; 1982. 69 p.

Manning, J. R. NBS: materials measurements. Nat. Bur. Stand. (U.S.) NBSIR 82-2560; in press.

### Sponsored Conferences

Process Control Sensors for the Steel Industry  
NBS, Gaithersburg, MD  
July 27-28, 1982  
R. Mehrabian, Member, Coordinating Committee

### Industrial Interactions

#### Other Industrial Guest Workers at CMS

Wuhan Research Institute of Materials Protection, Wuhan,  
Peoples Republic of China/Ximing Meng/A. W. Ruff

Work concerned the wear of steels of different chemical and mechanical properties. Results were a direct contribution to our Wear Durability Program, as well as to the guest worker's organization interests.

Archival Technical Papers Coauthored With Industrial Employee

Characterization of Wear Surfaces and Wear Debris/A. W. Ruff  
and L. K. Ives

W. A. Glaeser, Battelle Columbus Laboratories

Wear of Materials - 1981/A. W. Ruff  
S. K. Rhee, Bendix Research Laboratories  
K. C. Ludema, University of Michigan

Formal Visits to NBS by Industrial Management or Policy Making  
R&D Personnel or by NBS Managers to Industrial R&D Sites

Montreal Engineering Co./October 21, 1981  
Discussed erosive wear measurement techniques and apparatus  
designs, including new standard method.

Anaconda Industries/October 27, 1981  
Visited NBS to discuss Diffusion in Metals Data Center and  
diffusion in copper alloys.

Artech Corp./November 2, 1981, November 30, 1981  
Visits have been exchanged with NBS on several occasions to  
discuss mutual interests in metal coatings.

Glacier Metal Corp./November 30, 1981  
Visited NBS to learn our wear test methods, wear data, and  
effects of metallurgical variables.

Anaconda Industries/February 22, 1982  
Discussed wear of metals (copper alloys) and appropriate  
methods for laboratory testing.

Fairchild Industries/February 24, 1982  
Visited NBS to discuss diffusion in alloys used for Sterling  
engines.

General Electric Research Lab./April 24, 1982  
Visited NBS to discuss galling wear and metallurgical effects.

International Business Machines/May 5, 1982  
Visited NBS to discuss grain boundary diffusion in metallic  
systems.

Bendix Advanced Research Lab./May 12, 1982  
Visited by A. W. Ruff to discuss wear testing methods.

Westinghouse Electric Corp./May 19, 1982  
Visited NBS to discuss wear test needs in U.S. and effect of  
environments on wear.

Hughes Research Laboratories/May 25 - June 4, 1982  
Visited NBS to discuss theory of phase transformations and  
interfacial energies.



Engelhard Industries/July 7, 1982  
Visited NBS to discuss rapid solidification and metals processing.

Continental Can Company/July 29, 1982  
Visited NBS to discuss galling wear in forming can shapes with dies.

Participation in Measurement Programs Involving Substantial Industrial Cooperation.

Participated in ASTM interlaboratory test series on erosive wear with personnel from Eastman Kodak, Union Carbide, Cabot Corporation.

Chairing newly formed task group on galling wear under Wear Subcommittee ASTM G-02 Committee on Erosion and Wear.

Microhardness Round Robin Test Participant for ASTM E-4.05 Subcommittee.

Participated in several round robins for ASTM with implant manufacturers.

In November 1981, participated in interlaboratory test series involving F746-82 Pitting and Crevice Corrosion Test Method with nine other laboratories, including Cabot Corp., Cardiac Pacemakers, Inc., Strauman Institute, Richards Manufacturing Co., Howmedica, Inc., and Zimmer U.S.A.

#### Data Programs with Substantial Industrial Support and/or Guidance

Agreement between International Copper Research Association (INCRA) and the National Bureau of Standards (NBS) that a 500 page volume prepared by the NBS Diffusion in Metals Data Center on "Mass Transport and Diffusion in Copper Alloys" will be published by INCRA as part of the INCRA Metallurgy of Copper Series. INCRA also shared in the costs for the copper data evaluations and preparation of this manuscript.

The Alloy Phase Diagram Data Center within the Chemical Metallurgy Group works closely with the American Society for Metals under the joint ASM/NBS agreement. Technical evaluations and reviews of the alloy phase diagram data are performed at NBS and published in the Bulletin of Alloy Phase Diagrams by ASM. Financial support and guidance from industry is sought by ASM.

#### Formal Advisory Activities for Industrial Institutions

A. W. Ruff is a member of the Technical Advisory Committee for the Metals Properties Counsel.

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## REACTOR RADIATION DIVISION (566)

Robert S. Carter, Chief  
Tawfik M. Raby, Deputy Chief  
T. L. Mangum, Secretary

The National Bureau of Standards reactor (NBSR) is a national center for the application of reactor radiation to a variety of problems of national concern. The major areas of activity are:

Materials Characterization  
Nondestructive Evaluation  
Trace Analysis  
Radiation Standards and Measurement

The Reactor Radiation Division (RRD), in collaboration with other scientists within the Center for Materials Science (CMS), and other NBS Centers, and outside organization conducts long term research using neutron scattering methods to determine the properties and behavior of materials at the atomic level. These methods are used to study a wide variety of problems such as hydrogen in metals, the microstructure of rapidly solidified materials, microscopic properties of advanced crystalline and amorphous magnetic materials, polymers, molecular species and interactions on catalytic surfaces, and the structure of biological molecules. These measurements have wide generic applications to understanding of hydrogen embrittlement of metals, alloys and magnetic materials, ceramics and fast-ion conductors, polymeric structure, chemical catalysis, and biological processes. NBS is in an unique position to carry out such a multidisciplinary program because of its strong materials programs centered in CMS and other centers and its unique reactor facilities that are not available in industrial laboratories.

In the area of nondestructive evaluation (NDE), RRD uses neutron radiography and both large and small-angle neutron diffraction to examine objects for defects or hidden components that must be examined nondestructively. The major effort is in the development of neutron methods for nondestructive evaluation. Methods are being developed for such diverse applications as the use of autoradiography to study rare paintings and the use of neutron scattering to investigate the properties of rapidly solidified alloys. This program is partially funded through the Office of Nondestructive Evaluation and is part of the Bureau-wide effort to improve productivity through better quality assurance and increased component lifetime.

Neutron activation analysis is a very sensitive technique for measuring trace elements at very low concentrations. RRD provides the sample irradiations, but the program and sample analysis is carried out by the Center for Analytical Chemistry. It is used extensively for characterizing Standard Reference Materials (SRM) and a variety of other measurements such as the determination of impurities in solar cell materials and environmental studies. A large number of outside organizations also use this technique for measuring trace elements or pollutants in foods and drugs, environmental samples, criminal artifacts, etc. This is one of the largest neutron activation analysis activities in the country with many thousands of samples irradiated each year. Although the



primary effort in this activity is centered around neutron activation analysis, other neutron analytical methods are also being developed. A facility has been built to analyze for trace elements by measuring the prompt gamma ray spectrum induced by neutron capture in the sample, and a method has been developed (depth profiling) to measure concentrations of light elements as a function of depth with 100 Å depth resolution.

The program in radiation standards and measurements is carried out by the Center for Radiation Research (CRR). Through the use of double fission chambers and a series of accurately calibrated fission foils, they provide the basis for reactor neutron flux and power density measurements needed in the U.S. fast-flux development program. The calibration and intercomparison of the series of fission foils makes use of standard reference neutron fields established in the thermal column of the NBSR. CRR also maintains well characterized, filtered neutron beams in the reactor of 2 keV, 25 keV, and 144 keV energy for the calibration and development of personnel neutron dosimeters.

A number of other programs both within and outside NBS utilize the long-term irradiation facilities at the NBSR for activities ranging from γ-ray and x-ray physics and standards to applications of isotopes in medical diagnosis.

As is indicated above, RRD has a dual function. It conducts research programs in the areas of materials characterization and nondestructive evaluation and serves as a focal point of neutron scattering expertise for many other programs within and without the Bureau. The second function includes not only the operation of the reactor, but also providing sample irradiation services for a large number of users.

An important part of the overall Reactor Radiation Division's contribution to the NBS mission and to the scientific and technical community is in fostering the utilization of the reactor by other NBS groups and outside organizations. Interactions with other scientists and organizations take the form of both collaborative efforts and independent programs which rely on utilization of the reactor and facilities provided by the NBSR staff. The extent of such interactions for FY82 are indicated in the tables below. The number of personnel shown in tables 1 and 2 include many short-term collaborators as well as permanent other agency and university guest workers. These numbers are constantly changing and so may not be exact.

Collaborative interactions are those in which workers from outside the RRD collaborate scientifically with RRD scientists on problems of mutual interest. These interactions are summarized in table 1.

These tables demonstrate the extensive utilization of the NBS reactor by scientists and engineers from outside the Division. They come from 18 NBS Divisions and offices, 30 Government and industrial laboratories, and more than 20 universities.

Many of the other agency and university collaborators have worked with us regularly for many years. Five of them (two from the Navy and three from the Army) are assigned to work full time at the reactor on a permanent

Table 1. Collaborative Interactions

	<u>No. of Personnel</u> FY82
RRD Permanent Scientists	12
Non-RRD Participants	
Other NBS	22
Other Agency	32
University	27
Industrial	<u>12</u>
Total Non-RRD	93

Independent programs are those programs carried out independently of the Reactor Radiation Division scientific staff by other NBS Divisions and outside organizations. Table 2 summarizes these interactions.

Table 2. Independent Programs

	<u>No. of Personnel</u> FY82
Other NBS	28
Other Agencies	23
Universities	17
Industrial	<u>4</u>
Total	72

basis. Others regularly spend two or three days a week at the reactor. Bureau collaborative programs include measurements on fast-ion conductors, polymers, catalytic materials, hydrogen embrittlement, voids and precipitates in alloys, etc.

The two major independent (non-collaborative) Bureau programs are trace analysis by neutron activation analysis run by the Center for Analytical Chemistry and standard neutron fields for neutron flux calibration and materials dosimetry in the Center for Radiation Research. Although these activities are included in more detail with all the other activities at the reactor in the reactor annual report, NBS Reactor: Summary of Activities,<sup>1</sup> a few highlights will be given here.

The neutron standards and dosimetry program utilizes three filtered neutron beams, one thermal beam from the thermal column, and a cavity in the thermal column in which they can establish several types of well-characterized neutron fields. Typical projects include:

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<sup>1</sup>Copies of this summary for July 1981-June 1982 will be made available to Panel Members prior to the meeting.

- Intercomparison of flux parameters for filtered beams at the NBS reactor with those at Physikalisch-Technische Bundesanstalt, the West German Standards Laboratory at Braunschweig.
- Fission cross section measurements in the Intermediate-Energy Standard Neutron Field (ISNF) for U-233, Pu-240, Pu-241, and Th-232.
- Quality control tests for Navy shipboard area neutron dosimetry monitors.
- Systematic performance testing of essentially all types of personnel neutron dosimeters used in the U.S.
- Preparation of neutron fluence standards at the cavity fission source for calibration of a dosimetry counting system at Oak Ridge National Laboratory, TN.

The neutron activation analysis program primarily uses the irradiation services of the reactor to irradiate samples for trace analysis. They also develop other analytical neutron methods. Only the most recently developed one, depth profiling, will be summarized.

Depth profiling is the determination of the amount and depth profile of elements such as helium, lithium, and boron in metal and semiconductor substrates. The depth distributions of such elements are of interest for first-wall fusion reactor design and for diffusion into metals. The distribution of lithium and especially boron in semiconductors is, of course, of great concern to the electronics community.

The depth profiling technique using thermal neutron beams involves illuminating a target with a beam of thermal neutrons and measuring, with an energy-dispersive detector (silicon surface barrier), the energy distribution of the charged particles produced. Since the incident neutron energy is completely negligible compared to the reaction Q-value ( $E_0$ ), the charged particles produced are both monoenergetic and isotropic.

Those particles which escape from the sample lose energy along their exit path at a known rate  $dE/dx$ . The energy distribution of these particles at a fixed escape geometry is measured by a silicon surface barrier detector. When subtracted from the initial energy ( $E_0$ ), the energy loss distribution is obtained, which can be directly related to the depth distribution of the parent isotope via the known stopping power.

Sensitivities of  $10^{15}$  atoms/cm<sup>3</sup> and depth resolutions of 100 Å are obtainable.

An exploratory project was initiated in this area three years ago and has now reached fruition in an excellent facility using a dedicated beam at the reactor. A high quality neutron beam with an intensity of  $3 \times 10^8$  n/cm<sup>2</sup>-s is achieved using a room temperature filter of 20 cm of sapphire and 8 cm of silicon single crystals. Characterization of the facility is now underway.



The Nuclear Regulatory Commission's (NRC) review of the NBS 20 MW license application continues slowly. The Draft Environmental Statement mentioned in last year's report to the Panel was issued for public comment by the NRC in January 1982. A few comments were received, mostly from other agencies. These have been addressed and the final Environmental Statement will probably be issued some time in September. The other report that must be completed by NRC is the Safety Evaluation Report (SER) on which work was begun in July 1982 after a six-month delay. The final license is not expected before January 1983.

The procurement of reactor fuel from the new vendor, Babcock & Wilcox, appears to be on schedule. They have completed their facilities on schedule and are already assembling some fuel elements for NBS.

The scientific work of the Reactor Radiation Division and its collaborators is summarized later in this report and details are given in the Summary of Activities mentioned above. A few highlights will be given here to indicate the current direction and accomplishment of the Division.

During the past year, as part of the Division's Advanced Neutron Methods competence initiative, the NBS small-angle neutron scattering (SANS) facility has become fully operational, with the installation of the 64 x 64 cm detector along with the implementation of computer-controlled systems for automatic sample changing (up to four samples) and temperature control, and further development of data analysis and display programs linked to the technicolor graphics system. A great deal of exciting new SANS research has been carried out, ranging from the first direct observation of microcracks in bulk ceramics, to studies of polymer-surfactant interactions with industrial scientists, to the nondestructive evaluation of creep-induced cavitations in stainless steel. This extensive work has involved cooperation with four CMS Divisions, seven industrial and Government laboratories and ten universities from the U.S. and abroad. In the area of inelastic scattering, our new neutron time-of-flight facility has become fully operational, and experiments have been initiated on the investigation of chemisorbed species on metal particles, and on the phonon spectra of hydrogen dissolved in metals.

Major accomplishments in our other research and measurement tasks include a systematic study of the vibration spectra of hydrogen isotopes in palladium down to the 0.2 percent level, which provides: (1) an anomalous isotope shift in the solute ( $\alpha$ ) phase which is the same as that observed for superconducting ( $\beta$ -phase) palladium hydride and may have an impact on the theory of superconductive behavior in palladium alloy hydrides and (2) observation for the first time of an anomalous phonon splitting due to a chemically equivalent light atom defect in a metal. In addition, previous RRD neutron measurements on hydrogen trapped by atomic oxygen and atomic nitrogen impurities in niobium have allowed establishment of an atomic scale trapping mechanism decidedly different than those previously proposed. Neutron scattering investigations with the Center for Chemical Physics of chemical species and reactions on metal catalysts has been extended to studies of carefully processed platinum particles and have led to discovery of, for example, different binding states for hydrogen chemisorbed on "unperturbed" platinum sites compared to sites

containing oxygen impurities. Continuing research on magnetic and amorphous alloys in cooperation with the Naval Research Laboratory (NRL) and Bell Laboratories has established the existence of highly anisotropic propagating magnetic modes in  $\text{HoAl}_2$  and has shown that two kinds of magnetic order exist within FeNi glassy alloys, each associated with a different time scale.

In continuing materials structure and database activities RRD has completed a number of essential studies of atomic scale structure and microscopic properties of prototype or tailored oxide compounds with generic application to small batteries and other electronic applications (in cooperation, with the Materials Chemistry Division, Bell Laboratories, and Massachusetts Institute of Technology); corrosion inhibitors (with 3M Co.); electrolytic products related to storage-battery lifetime; zeolyte catalysts (with E. I. Dupont de Nemours, Inc.); and cancer drugs (with the Food and Drug Administration). Systematic x-ray or neutron studies have also been used to study the effects of compressive stress on the separate components of bulk composites (Si-Al), and as part of an effort to identify critical feedstock properties for quality control in the production of cellulose compounds. In the Crystal Data Center this past year, a formal agreement was established with the International Centre for Diffraction Data to expedite transfer of the Crystal Data Identification file to the chemical and materials communities via magnetic tapes, designed a new matrix method for critical evaluation of symmetry, and added 2000 metal and intermetallic data entries to the master database. Finally in a joint effort with the Smithsonian Institution to develop neutron-autoradiography methods, design of a major new facility with extremely high neutron to x-ray intensity ratios has been completed and several test radiographs on rare art works have been accomplished.

Plans for the coming year include expanded work in the development of SANS as a nondestructive probe of distributed damage (voids, cracks, segregations) in bulk metals and ceramics and continued emphasis on cooperative research with other CMS Divisions and industrial labs on using neutron methods for applications in processing science and durability, including a first attempt to study the atom scale behavior of hydrogen at  $< 10$  ppm in iron and steel. Emphasis will also be given to fundamental studies of short-range order, transformations and spin dynamics of technologically attractive amorphous alloys and spin glasses, using SANS and high-resolution inelastic scattering methods. Cooperative research on catalytic reactions on metal surfaces will be extended to attempt unique measurements of metal surface vibrations and the rotational behavior of molecular fragments. Finally in the data programs, publication of two volumes of Crystal Data for organic materials is anticipated.



REACTOR OPERATIONS AND SERVICES  
Task 12161

The reactor was operated on a normal round-the-clock schedule for the entire year. Other than scheduled shutdowns for maintenance, refueling, testing, and for staff vacation, there were no interruptions in the operating schedule. A program of modernization of reactor components and instrumentation which started last year is continuing. Licensing activities to upgrade reactor power to 20 MW and renew the operating license are progressing. A Draft Environmental Impact Statement has been published by the Nuclear Regulatory Commission as required by regulations. A final statement will be issued later this year. The NRC is also preparing a safety evaluation report of the NBS submittals. In this connection NBS provided extensive additional information to NRC to assist in their review. A new license will be issued by the NRC, once the Environmental Impact Statement and the Safety Evaluation Report are published. The new license authorizing increased power and valid for a period of 20 years is expected in early 1983.

Utilization of the reactor continued to be extensive and wide-ranging. More than 125,000 instrument hours involving 25 simultaneously operable experimental facilities have been provided to more than 50 organizations from within and outside NBS.

Reactor Operations  
Subtask 1 of Task 12161

T. M. Raby and J. F. Torrence

Over the past year, the reactor was on-line nearly 80 percent of the time and operating at full power 73 percent of the time. This is about the maximum efficiency that can be achieved with the available staff. Once again a remarkable improvement in fuel utilization efficiency was realized by use of new higher loaded elements. An efficiency increase of nearly 50 percent resulting in an average fuel burnup of 65 percent is the best in the history of the facility and has already resulted in a significant fuel cost savings. A summary of the overall operating statistics for the period July 1, 1981 to June 30, 1982 is presented in the following table.

NBSR Operating Summary FY81

Number of days at 10 MW	268
On-line time at 10 MW	73%
Average U-235 burnup	65%
Number of Irradiations	3450
Hours of Irradiations	3100
Hours per Irradiation	0.9



Irradiation Service  
Subtask 2 of Task 12161

N. A. Bickford and J. H. Ring

Heavy utilization of the reactor for activation analysis and irradiation services continued this year. The number of irradiations increased by more than 30 percent. Tens of thousands of specimens, involving foods, drugs, environmental monitoring, geological and mineral examinations, forensic investigation, and development of standard reference materials were irradiated at the NBS reactor.

Engineering Services  
Subtask 3 of Task 12161

J. H. Nicklas and R. S. Conway

In addition to regular engineering and design services provided to reactor operations, experimenters, and users, the engineering staff was involved in a comprehensive program of reactor modernization. A contract has been signed for a fire suppression system for the new cooling towers. The water treatment building and loading ramp for chemical treatment of the secondary water has been out for bid and is in the negotiation stage. A contract to fabricate new shim arm poison blades has been let. Tooling for this type of control rod was developed and used at Argonne National Laboratory and will be used for this fabrication. Shim arm yokes, arbors and bearings are in the process of fabrication. Redesign of the regulating rod for 20 MW operation has begun which will provide a smoother and more reliable regulating rod operation. A new fuel element contractor has been selected by the Department of Energy (DOE) and has made an NBSR prototype fuel assembly and a production prototype. Fabrication of actual fuel assemblies will begin when parts have been received from the sub-contractor.

Extensive effort was expended to implement the modernization program for the reactor instrumentation. This program replaces old equipment with more modern reliable console readout devices. For example, the miniature process recorders provide a faster response indication with the benefit of easy-to-replace ink cartridges and a much simpler chart roll cassette. The nuclear indication has been expanded to provide the operator with a console meter for each power range and recorded information for both start-up channels and intermediate channels continuously.

Nuclear power supplies were replaced by updated versions that meet all the safety and reliability requirements of the old ones and, in addition, provide over-current and over-voltage protection. The replacement of individual shim arm position indicators provides the operator with a readout capability of 1/100 of a degree.

## NEUTRON SCATTERING CHARACTERIZATION OF MATERIALS FOR ADVANCED TECHNOLOGIES Task 12162

This task develops and applies advanced neutron scattering methods and related theoretical analysis for research on the microscopic properties of materials which affect their use in technological applications. Current areas of emphasis include hydrogen in metals, new magnetic and glassy materials, and catalytic materials. The neutron inelastic, quasielastic, and magnetic scattering techniques applied provide unique information, for example, on: phase transformations; interatom bonds; electronic structure; sublattice magnetization; hydrogen binding, trapping, and diffusion; and molecular and crystal dynamics. The members of this task (and the following task) are also responsible for establishing and maintaining a center of excellence for neutron scattering and radiographic measurements including a computer-controlled network of ten spectrometers at the reactor. Task scientists couple directly with other NBS and outside groups who require state-of-the-art neutron measurement methods and expertise in their programs. Examples include long-term collaborative efforts with in-house guest workers from Army Materials Command, Naval Research Laboratory, the Naval Surface Weapons Center (NSWC), and the University of Maryland on materials for improved microwave transmission and sonar and advanced explosive formulations; cooperative fundamental research with industrial scientists (Allied Chemical Corporation, Bell Laboratories) on new classes of materials with potential applications for advanced power transformers, computers, and energy storage; and research on hydrogen in metals, intercalation compounds, and prototype phase transformations in solids with other national laboratories (Argonne National Laboratory; Brookhaven National Laboratory; National Research Council, Canada) and universities (University of Illinois; University of Pittsburgh; University of Vermont; Cornell University; University of Antwerp; University of Munich). In addition, staff scientists are actively engaged with other Divisions and Centers at NBS in the application of neutron scattering methods for (1) surface analysis of chemical products and reactions on industrial catalysts, (2) ultrasensitive microscopic analysis of hydrogen in metals, and (3) computer simulation of chemical reactions in condensed phases.

### Microscopic Properties of Hydrogen in Metals and Molecular Materials Subtask 1 of 12162

J. M. Rowe, J. J. Rush, R. C. Casella, S. F. Trevino<sup>1</sup>

<sup>1</sup>Guest Worker, Army Armament Research and Development Command (AARADCOM)

#### Hydrogen in Metals

As part of its program of unique studies of vibration spectra and atomic-scale behavior of hydrogen in metals down to the 0.1 percent level, this group (in collaboration with guest workers from the University of Munich, Institut Laue-Langevin, and University of Illinois) has extended research on hydrogen trapped by impurities to intermetallic systems (TiCr, Pd<sub>3</sub>Mn) and completed an extensive study of H and D isotopes in palladium down to 0.2 percent H. Previous NBS measurements on hydrogen trapped by interstitial atomic oxygen and atomic nitrogen in niobium have been



utilized to propose a trapping mechanism which is decidedly different from those proposed on the basis of macroscopic measurements. Associated with these experiments, theoretical work is being carried out to elucidate the role of elastic strain, H-H interactions, and relaxation effects on the details of the hydrogen vibration spectra and to study the effects of band formation by low concentrations of H in pure metals. The neutron spectra for the  $\alpha$ - and  $\beta$ -phase  $\text{PdH}_x(\text{D}_x)$  have yielded several highly

interesting results: (1) an anomalous isotope shift is observed for hydrogen vibrations in the  $\alpha$ - (solute) phase which is the same as that observed for  $\beta$ - $\text{PdH}(\text{D})$ , which may have an impact on current theoretical interpretation of the high-temperature ( $\sim 10$  K) superconducting transition observed for palladium hydride near stoichiometry; (2) the optical vibrations of  $\alpha$ - $\text{PdH}_x$  show no measurable change for  $x$  between 0.002 and 0.02, and thus show no evidence of hydrogen clustering in  $\alpha$ -palladium proposed on the basis of earlier neutron work; (3) the neutron spectra  $\beta$ -phase palladium deuteride diluted with a small amount (3 percent) of H provides, for the first time, a direct measurement of anomalous phonon splitting due to a chemically equivalent light atom defect in a metal. Other results during the past year include the observation of diffuse peaks in the diffraction pattern of  $\alpha$ - $\text{VD}_{0.8}$ , which can be directly interpreted as "lattice liquid" distribution of deuteriums within the regular bcc metal structure. In addition, we are currently designing an experiment to test the utilization of these highly sensitive measurement capabilities to probe hydrogen at embrittlement levels ( $< 10$  ppm) in iron and steel.

#### Disordered and Catalytic Materials

We have continued our theoretical and neutron scattering studies on the microscopic properties and novel phases of prototype solids exhibiting orientational disorder associated with local strains and anomalous elastic behavior. A new theory is being developed to explain the absence of observable optical modes in alkali cyanides, which includes the effects of asymmetry (electrical and mechanical) of the CN<sup>-</sup> ion and the interaction of the optical vibrations with the hindered rotational states of the linear ions. Both experimental and theoretical studies have continued of the novel "quadrupole glass" state proposed for KCN-KBr mixed crystals from our previous neutron scattering work. Recent articles have questioned the existence of a real transition to such a state in these materials, based on observed dielectric behavior. However, our recent analysis shows conclusively that the alternative explanation of orientational behavior in these compounds (a gradual "freezing in") is totally inconsistent with the neutron data and thus very likely an incorrect interpretation of the dielectric results.

Our collaborative research effort with the Surface Science and Molecular Spectroscopy Division on neutron scattering investigations of chemical species and reactions on fine-particle metallic catalysts has been extended to systematic studies of chemisorption on carefully processed platinum catalysts under relevant temperature and pressure conditions. Different binding states have been found for hydrogen chemisorbed on "unperturbed" platinum sites compared to sites containing oxygen impurities near the surface. Studies of adsorbed ethylene and acetylene as a function of temperature reveal the creation at temperatures  $> 150$  K of a



more highly saturated hydrocarbon species, possibly analogous to methylated species suggested from electron scattering studies on single crystals of platinum under ultrahigh vacuum conditions. Recently we have also completed our first studies of the low-frequency (0 to 10 THz) dynamics of the platinum catalysts with ethylene surface layers, using the new NBS time-of-flight neutron spectrometer. These studies are being pursued in an attempt to probe directly the rotational behavior of hydrocarbon fragments on metal catalysts.

Finally, in cooperative research efforts with Army guest workers and the Center for Chemical Engineering on computer simulation of chemical reactions in condensed materials, this group has simulated both the equilibrium and nonequilibrium behavior as a function of temperature and the energy transfer mechanisms of model dimers bound in the solid state. This work is intended to establish a predictive capability for fast chemical interactions in molecular solids under conditions far from equilibrium (e.g., in a shock wave).

#### Microscopic Properties of Magnetic and Amorphous Materials Subtask 2 of Task 12162

J. J. Rhyne, J. Lynn,<sup>1</sup> H. Alperin,<sup>2</sup> R. Erwin,<sup>3</sup> J. Fernandez-Baca<sup>3</sup>

<sup>1</sup>Consultant, University of Maryland

<sup>2</sup>Guest Worker, Naval Surface Weapons Center

<sup>3</sup>Guest Worker (Graduate Student), University of Maryland

This subtask provides a focus for application and improvement of neutron elastic and inelastic scattering techniques for fundamental studies of the microscopic properties of new classes of metallic and magnetic materials (including rare earth metal compounds, magnetic hydrides, and amorphous and spin glass materials), many of which exhibit novel properties of potential use in device applications and high-technology products. This research is carried out in close collaboration with industrial laboratories, universities, and other CMS scientists.

During the past year, research emphasis in the subtask was placed on (1) spin dynamics of the rare earth Laves phase alloy  $\text{HoAl}_2$ , which exhibits a strong interplay of exchange and crystal field interaction energies (collaboration with NRL); (2) dynamics and critical properties of a class of amorphous metal alloys, which exhibit coexistence phenomena of ferromagnetism and spin glass states, and a reentrant spin glass state at low T (collaboration with Bell Laboratories and the University of Maryland); (3) expanded studies of  $\text{Fe}_x\text{B}_{1-x}$  amorphous alloy spin

dynamics and local and intermediate range atom-atom correlations, including additional compositions exhibiting the Invar anomaly and a study of the unusual temperature renormalization of the spin stiffness found for these prototype soft magnetic alloys (collaborative research with Allied Chemical Corporation and NRL); (4) extended measurements of small-angle magnetic scattering in coexistent superconducting-magnetically ordered compounds below 1.5 K (collaboration with the University of Maryland); (5) detailed analysis of the atomic structure correlations in rapidly solidified  $\text{TbFe}_2$  and  $\text{YFe}_2$  alloys to examine correlations higher than pair-pair interactions (collaboration with NRL); and (6) studies of the

microstructure, short-range order, and transformations of metallic glasses and "glassy" carbon as a function of high-temperature annealing [in cooperation with the Metallurgy Division and the University of California (Berkeley)].

Highlights during the past year include:

- Established the existence of propagating magnetic modes of highly anisotropic character in  $\text{HoAl}_2$  and determined the effect of the large crystal field interaction of the exchange splitting of states in this compound.
- Confirmed an anomalous  $T^{5/2}$  power temperature renormalization of the spin wave stiffness parameter in two amorphous  $\text{Fe}_x\text{B}_{1-x}$  compound compositions and examined the unusual departure of the spin stiffness constant from that calculated from the magnetization.
- Extended results on small-angle magnetic scattering in  $\text{TbFe}_2$  and  $\text{YFe}_2$  to  $0.15 \text{ \AA}^{-1}$  and confirmed the absence of a conventional second order phase transition at  $T_c$  and the existence of microdomain order below  $T_c$ .
- Initiated a study of the effect of composition and heat treatment on the magnetic structure of amorphous metal alloys and a correlation of the results with changes in their magnetostructure behavior.
- Established the existence of two time-scales in the magnetic order of  $\text{Fe}_x\text{Ni}_{1-x}$  glassy alloys--one related to the statics as manifested by a resolution-limited elastic scattering peak and a second significantly shorter time-scale associated with the spin excitations.
- Examined the coexistence of a superconducting and ferromagnetic state in the compound  $\text{Er}_{0.1}\text{Ho}_{0.9}\text{Rh}_4\text{B}_4$  and the magnetic behavior in the vicinity of the multicritical point.



## NEUTRON STRUCTURE METHODS AND CRYSTAL DATABASE FOR MATERIALS UTILIZATION AND DURABILITY

### Task 12163

This task utilizes the unique properties of neutrons (deep penetration capability, sensitivity to light atoms, and well-defined lineshapes for precise structure analysis) to extend basic cutting edge measurement capabilities in the structural analysis and nondestructive testing of materials. Task members have competences at the forefront of measurement and analysis of materials structure, including concentrated efforts in neutron powder diffraction, profile analysis methods, broad expertise in radiographic measurement technology, and state-of-the-art computer-controlled diffraction facilities. This expertise is used to develop advanced diffraction and radiographic methods and analytical techniques to provide: (1) precise structure analysis essential for effective use of materials (e.g., in batteries, chemical catalysis); (2) development and computerized transfer of evaluated materials structure database to industrial and scientific user community; and (3) nondestructive reference methods for defects, precipitations, and texture affecting metal product performance, for improved quality assurance, e.g., in composites, rapidly solidified alloys, and plant and field inspections and for microstructure analysis of materials under stress. Current research and measurement activities include cooperative projects with four CMS Divisions (Materials Structure and Durability) and the Center for Radiation Research. This task also directly serves the Offices of Nondestructive Evaluation and Standard Reference Data. Outside interactions and cooperative research with groups needing advanced neutron methods include National Institutes of Health (NIH); Naval Research Laboratory; Army Materials Command; U.S. Navy Department; Food and Drug Administration; Smithsonian Institution; Allied Chemical Corporation; Bell Laboratories; E. I. Dupont de Nemours, Inc.; Metronics, Inc.; Union Carbide Corporation; 3 M Co.; and universities on projects ranging from crystallographic database development to the structure of proteins.

### Neutron Diffraction Methods and Applications

#### Subtask 1 of 12163

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<sup>1</sup>Guest Worker, AARADCOM

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Recent improvements in refinement methods and lineshape analysis for powder diffraction developed by this group continue to greatly enhance research and applications on the structure and microscopic properties of complex inorganic materials. During the past year, a great deal of work has been completed on the structure of prototype or tailored oxide compounds whose novel ionic or electronic conductivity are of interest in the development of more efficient or smaller batteries or in other electronic applications. These efforts include determination of the structure and conduction paths in lithium-based tantalate or vanadate compounds with scientists from Bell Laboratories, the University of Grenoble, and the Materials Chemistry Division and studies of the



composition dependence of conductive channels in sodium superionic conductor (NASICON) solid solutions, which are linked three dimensionally in the structure and provide conductivities at 300 °C comparable to  $\beta$ -alumina. In addition, a series of investigations have been completed (with NRL) of the structure of  $\beta$ -phase  $\text{PbO}_2$ , both chemically produced and extracted from lead storage batteries after varying degrees of electrolysis. These studies are aimed (along with chemical tests) at providing detailed information on the factors (including impurity phases), which influence battery lifetime and performance. Among other applications, diffraction techniques have been used to determine the structure of copper complexes of the corrosion-inhibitor benzotriazolate in cooperation with 3M Research Laboratory, to study the hydrogen bonds in complex phosphates with the Polymer Division's dental research group, to determine cancer drug structures with the American Dental Association, and in a preliminary study, in collaboration with E. I. Dupont de Nemours, Inc., of structure and cage geometry in zeolyte catalysts.

In the past year, neutron diffraction methods have also been used in several metallurgical and NDE applications. In cooperation with the Polymer and Metallurgy Divisions, we have initiated a study of the effects of interstitial elements on phase relationships in Ti-Al alloys, which will ultimately be carried to 1500 K. In addition, we have demonstrated with the Naval Surface Weapon Center the feasibility of using neutron diffraction as a tool for studies of the effects of compressive stress on the separate components in a composite material (SiC-Al).

In our long-term collaborative program with Army guest workers on the structure and properties of metastable materials this subtask has (1) completed a series of x-ray line profile analyses of structural differences in cellulose produced from cotton linter and less costly wood pulp. This is part of an effort to identify critical feedstock properties for quality control which would allow production of cellulose compounds from more readily available wood pulp sources; and (2) determined the structure of the low temperature phase of ammonium nitrate to complete a long-term study of all of the phases of this compound.

Finally, in the NBS-NIH collaborative project on the structure of biological materials, our group has completed collection of neutron and x-ray data on ribonuclease enzyme doped with a vanadium complex to simulate the conditions which exist on a molecular scale during biocatalysis involving this enzyme. A study has also been initiated in collaboration with the University of Peking of the structure of insulin (to obtain detailed information on the roles of H bonds in the structure).

NBS Crystal Data Center  
Subtask 2 of 12163

A. D. Mighell, J. K. Stalick, V. L. Himes<sup>1</sup>

<sup>1</sup>NBS Coop Student from Catholic University

The Crystal Data Center collects, evaluates, and disseminates to the industrial and scientific community crystallochemical data that are required for the identification and characterization of solid-state materials. The work of the Center is carried out in close collaboration

with allied data centers in the United States, England, Canada, and the Federal Republic of Germany. A major recent objective is to build a computer-based Master Data File around which all operations are based.

Accomplishments during the past year include:

- The establishment of a formal agreement with the International Centre for Diffraction Data and the Joint Committee on Powder Diffraction to expedite collection of crystal data and the marketing of the Crystal Data Identification file to the chemical and materials community via magnetic tape.
- Approximately 2000 entries with metals and intermetallic data have been added to the Master Database and an on-line search system for the Crystal Data File was implemented by the Chemical Information System. In addition, format specifications for Volumes 5 and 6 of Crystal Data were completed.
- In our research efforts on crystallographic analysis and evaluation, a new matrix method for critical evaluation of symmetry was designed and tested and a program for calculation of densities from atomic volumes was incorporated into the data system.

#### Radiographic Methods and Standards

##### Subtask 3 of Task 12163

D. A. Garrett, M. Ganoczy, and Y. T. Cheng<sup>1</sup>

<sup>1</sup>Guest Worker, Smithsonian Institution

Due to staff reduction and extensive illness within the group, the activities of this subtask were somewhat curtailed. Significant progress, however, was made towards the development of neutron autoradiographic methods. In particular, the joint program with the Smithsonian Institution in the autoradiography of paintings continued to develop. The design of a major facility to be installed at the thermal column has been completed. A preliminary experimental setup was used to obtain autoradiographs of a sixteenth century Russian icon and a nineteenth century painting by Dewing, a well-known American artist. These series of autoradiographs demonstrated the value of this method in the study of valuable paintings. Neutron autoradiography provides a nondestructive means to analyze chemical composition of pigments in place, and thus for example help in validation of original art works, and locates overpainting by the artist.

A variety of other tasks was completed. Preliminary work in cooperation with the Naval Research Laboratory was undertaken to explore the possibility of obtaining tomographic-type information from a series of radiographs taken as the object was rotated. Several feasibility studies were made including:

- Identification of loose plastic material in gyroscopes

- Determination of oil levels in accumulators used in missiles
- Search for hidden cracks in turbine blades
- Void density in composite binding material

In addition, film exposure curves were determined for a standard neutron beam conditions and a variety of converter screens.



## ADVANCED NEUTRON METHODS Task 51102

C. J. Glinka, N. Berk, J. LaRock, J. M. Rowe,<sup>1</sup> S. Singh<sup>2</sup>

<sup>1</sup>Competence Leader from Task 12162

<sup>2</sup>IPA Fellow

This task is one of the NBS competence building initiatives whose objective is to develop and maintain state-of-the-art facilities for advanced neutron scattering techniques and contribute to effective application of these facilities and techniques in solid-state physics, metallurgy, polymer science, and biology. The original focus of this initiative is on providing new major facilities for SANS and high-resolution, low-wave vector, inelastic scattering. With small-angle neutron scattering, one can probe structural entities and defects and inhomogeneities on the 10 to 3000 Å scale, while high-resolution, inelastic studies allow the observation of dynamic phenomena with characteristic times as low as  $10^{-10}$  s and spatial regions of 1 to 100 Å. The new facilities (which provide a world-class capability for NBS in these areas) will serve a wide variety of materials science and measurement programs within NBS, including polymer and surface science, materials microstructure and durability, nondestructive testing, and properties of fluids and solutions. New science and applications to be developed range from unique studies of the structure of polymers, high-technology magnetic glasses, and catalysts to the precise measurement of bulk microstructure in industrial materials and products under environments experienced in production and service. Close cooperation with a number of divisions within CMS and the Center for Chemical Physics (CCP) is an essential part of the Advanced Neutron Method Task, as is wide-ranging cooperative research and measurement activities with other Government laboratories and with a number of industries and universities.

### Summary of Activities

#### Facilities

During the past year, the 64 x 64 detector has been installed in the SANS facility and is now fully operational. The operating characteristics of the SANS instrument are now well-established, and the results are generally in accord with the original calculations, i.e., a neutron flux at the sample of from  $10^4$  to  $3 \times 10^5$  n/cm<sup>2</sup>/s under the highest and lowest resolution conditions respectively. These numbers will double when the reactor power increases to 20 MW next year. In addition, we have installed an automatic sample changer (computer-controlled), which can cycle up to four samples into the beam while the system is evacuated, and computer-controlled cryogenic and furnace sample environmental chambers. These enhancements have greatly increased the efficiency of utilization of the facility. We have also adapted horizontal and vertical field electromagnets to provide up to 10 kilogauss fields at the sample position. Data analysis and display programs have been developed to allow rapid assessment of data as it is taken, utilizing an interactive color graphics imaging system which allows easy visual assessment of the data. This capability is unique to the NBS

SANS facility. The neutron time-of-flight facility also became operational during the past year, and the signal-to-noise ratio has been increased significantly to the point that even difficult experiments are now possible. The data acquisition hardware and software are fully operational, and several experiments have been completed. Further planned upgrading to this facility includes new shielding, an evacuated flight path, additional detectors, better sample environmental facilities, and improved incident energy resolution. These improvements, combined with the reactor power increase to 20 MW, will make this a world-class facility.

#### Research and Measurement

The new state-of-the-art measurement capabilities associated with this Task have stimulated a number of exciting research efforts during the past year, particularly in the areas of polymers, metallurgy and ceramics, NDE, and in the physics of novel magnetic and glassy materials. A great deal of effort has been concentrated on establishing strong interactive research with other CMS Divisions (Polymers, Fracture and Deformation, Metallurgy) and with CCP, but our SANS and high-resolution inelastic scattering facilities have also been heavily utilized in cooperative research with outside industrial laboratories and universities, including Union Carbide Corporation; Exxon Chemical Company; Allied Chemical Corporation; Bell Laboratories; University of Wisconsin; University of Illinois; Northwestern University; State University of New York, SUNY; University of Maryland; and Institut Laure-Langevin, Grenoble, France, and with Government laboratories (NSWC, NRL, NIH).

Among accomplishments and initiated research and measurement efforts during the past year are:

- The first direct observation of size and density distributions of microcracks ( $< 1000 \text{ \AA}$ ) in bulk ceramics by SANS (Fracture and Deformation and Reactor Radiation Divisions).
- Measurement of the interaction of polymers and surfactants in solution (Polymer and Reactor Radiation Divisions and Union Carbide Corporation).
- Nondestructive evaluation of distributed damage and creep-induced cavitation related to component failure in stainless steel products (Reactor Radiation and Fracture and Deformation Divisions).
- Studies of magnetic microstructure and voids in maraging steel (Fracture and Deformation and Reactor Radiation Divisions).
- Investigation of magnetic and superconducting transitions in pseudo-ternary alloys and of magnetic clustering in amorphous  $\text{TbFe}_2$  (Reactor Radiation Division and University of Maryland).
- Completed initial measurements of low-energy spectra measured for hydrocarbon species trapped on the surface of metallic catalysts (Reactor Radiation Division and Center for Chemical Physics).

- Initiated systematic study of short-range order and transformations in TiCu metallic glasses (Reactor Radiation and Metallurgy Divisions with Allied Chemical Corporation).
- Initiated SANS study of spinodal decomposition in FeCr alloys (with Northwestern University).

Finally, a great deal of research on polymer chains and block copolymers in the solid state and in solution has been carried out by the Polymer Division in cooperation with scientists from the University of Wisconsin, University of Massachusetts, and with a number of Japanese guest workers.



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Other Activities of the  
Reactor Radiation Division

Invited Talks

Studies of Ribonuclease A by X-ray and Neutron Diffraction  
Chalmers Institute of Technology, Gothenburg, Sweden

A. Wlodawer  
November 3, 1981

Neutron Scattering Studies of Hydrogen in and on Metals  
Physics Department, Cornell University, Ithaca, NY

J. J. Rush  
December 2, 1981

Neutron Spectroscopic Studies of Dilute Hydrogen in Pure and Defected Metals

International Symposium on the Electronic Structures and Properties  
of Hydrogen in Metals, Richmond, VA

J. J. Rush  
March 5, 1982

A Procedure for Joint Refinement of Macromolecular Structures with  
X-ray and Neutron Single Crystal Diffraction Data  
American Crystallographic Association Spring Meeting, National Bureau  
of Standards, Gaithersburg, MD

A. Wlodawer  
March 31, 1982

The Structure of the Enzyme-Active Substrate Complex in Ribonuclease  
7th European Crystallography Meeting, Jerusalem, Israel

A. Wlodawer  
April 29, 1982

Translation-Rotation Coupling-Mixed Crystals of  $\text{KCN}_x\text{KBr}_{1-x}$

National Bureau of Standards, Surface Science Division,  
Gaithersburg, MD

J. M. Rowe  
April 1982

New Developments of the Rietveld Method. Applications to the Study  
of the Structure of  $\text{PbO}_2$  in Lead-Acid Batteries

Institute of Chemistry, Polytechnic of Milano, Milano, Italy

A. Santoro  
May 28, 1982

Joint X-ray and Neutron Refinement of Proteins  
Neutron Scattering Analysis for Biological Structure--Brookhaven  
Symposia, Upton, NY

A. Wlodawer  
June 3, 1982

New Developments of the Rietveld Method of Structural Refinement.  
Applications to the Study of Ionic Conductors  
University of Messina, Messina, Italy  
A. Santoro  
June 15, 1982

New Developments of the Rietveld Method of Structural Refinement.  
Applications to the Study of Ionic Conductors  
National Commission of Nuclear Energy, Rome, Italy  
A. Santoro  
June 27, 1982

Neutron Scattering Study of Magnetic Ordering in Ternary Superconductors  
Meeting on d- and f-Band Metals, Julich, Federal Republic of Germany  
J. W. Lynn  
June 1982

Assessing the Fit  
Powder Diffraction and Rietveld Analysis Workshop, Argonne National  
Laboratory, Argonne, IL  
E. Prince  
July 14, 1982

Non-linear Least Squares Fundamentals  
Powder Diffraction and Rietveld Analysis Workshop, Argonne National  
Laboratory, Argonne, IL  
E. Prince  
July 14, 1982

Constrained Refinement and Model Building  
Powder Diffraction and Rietveld Analysis Workshop, Argonne National  
Laboratory, Argonne, IL  
E. Prince  
July 15, 1982

High Resolution Neutron Diffraction of Proteins  
Gordon Conference on "Diffraction Methods in Molecular Biology,"  
Proctor Academy, Andover, NH  
A. Wlodawer  
July 30, 1982

#### Division Seminars

Transport in Amorphous Metals  
S. R. Nagle  
University of Chicago, Chicago, IL  
October 26, 1981

Computer Molecular Dynamics  
S. Yap  
MIT, Cambridge, MA  
November 6, 1981



Experience with Time-of-Flight Neutron Powder Diffraction at IPNS  
T. M. Sabine  
New South Wales Institute of Technology, Sidney, Australia  
December 21, 1981

Gamma Ray Scattering: Applications in Condensed Matter Science  
William Yelon  
University of Missouri, Columbia, MO  
February 2, 1982

Diffusion in Concentrated Lattice Gases  
K. Kehr  
Institut für Festkörperforschung der Kernforschungsanlage Jülich,  
Jülich, Federal Republic of Germany  
March 6, 1982

Temperature Dependence of the Structure Factor of  $\text{As}_2\text{Se}_3$  up to the  
Glass Transition  
L. E. Bussee  
University of Chicago, Chicago, IL  
March 23, 1982

Quadrupolar Interactions and Structural Instabilities in  $\text{PrAg}_x\text{Cu}_{1-x}$   
J. A. Gotaas  
University of Illinois at Chicago Circle, Chicago, IL  
March 26, 1982

Magnetic Properties and Applications of Amorphous Metallic Glasses  
R. Hasegawa  
Allied Corporation, Morristown, NJ  
April 21, 1982

Hydration in Aqueous Solutions  
Stewart Cummings  
Institut Laue-Langevin, Grenoble, France  
June 16, 1982

#### Technical and Professional Committee Participation and Leadership

American Crystallographic Association  
Apparatus and Standards Committee, E. Prince, Chairman  
Crystallographic Computing and Data Committee, A. Mighell, Liaison  
Officer  
Spring Meeting, Mathematics of Refinement Session, E. Prince,  
Session Chairman

American National Standards Committee  
N-17: Research Reactors, Reactor Physics, and Radiation Shielding,  
R. S. Carter, Chairman, T. M. Raby, Secretary

American Nuclear Society  
ANS-15 Standards for Research Reactors, T. M. Raby  
Standards Steering Committee, R. S. Carter, Voting Member

American Physical Society, Solid State Meeting (March)  
Amorphous Magnets Session, J. J. Rhyne, Session Chairman

American Society for Nondestructive Testing  
Penetrating Radiation Committee, D. A. Garrett, Voting Member  
Personnel Qualifications Committee, D. A. Garrett, Voting Member

American Society for Testing and Materials  
E-7.05: Nondestructive Testing--Neutron Radiography, D. A. Garrett,  
Secretary

Argonne National Laboratory  
Program Review Committee for the Intense Pulsed Neutron Source,  
J. M. Rowe, Chairman

Department of Energy  
Panel to Review U.S. Pulsed Neutron Scattering Research Facilities,  
J. J. Rush, Member  
Peer Review Panel for the Assessment of the Program in Basic Energy  
Sciences, J. M. Rowe, Member

Gordon Conference on Orientational Disorder in Crystals (1982)  
Reorientation Phenomena in Crystals Session, J. M. Rowe, Discussion  
Leader

Gordon Conference on Orientational Disorder in Crystals (1984)  
J. M. Rowe, Vice-Chairman

International Centre for Diffraction Data  
Data Base Subcommittee, A. D. Mighell, Member, J. K. Stalick,  
Member

International Conference on Magnetism (1985)  
Executive Committee, J. J. Rhyne, Publications Chairman

International Symposium on the Electronic Structure and Properties of  
Hydrogen in Metals  
International Organizing Committee, J. M. Rowe, Member  
Session VI, J. M. Rowe, Session Chairman

International Union of Crystallography  
Data Commission, A. D. Mighell, Member

International Union of Crystallography/National Bureau of Standards  
Crystal Data Management Board, A. D. Mighell, Member

National Academy of Sciences  
Panel on Synchrotron Radiation Facilities, J. M. Rowe, Member

National Bureau of Standards  
Library Committee, R. C. Casella, Subject Specialist

National Institute of General Medical Sciences  
Ad-hoc Study Section, A. Wlodawer, Member

Oak Ridge National Laboratory  
National Center for Small Angle Scattering Program Committee,  
B. Mozer, Member, J. J. Rhyne, Member  
Neutron Scattering User Program Advisory Committee, J. J. Rush,  
Member

Rare Earth Research Conferences  
Proceedings, J. J. Rhyne, Co-editor

27th Annual Conference on Magnetism and Magnetic Materials  
Amorphous Alloys III: Rare Earths Session, J. J. Rhyne, Session  
Chairman

### Publications

Brun, T. O.; Susman, S.; Rowe, J. M.; Rush, J. J. Quasielastic neutron scattering study of ionic diffusion in  $\beta$ -LiAl. Solid State Ionics 5: 417; 1981.

Casella, R. C. Detection of impurity tunneling in solids via coherent phonon coupling and direct neutron scattering. J. Phys. C 42: 923; 1981.

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Chen, H. S.; Lynn, J. W.; Erwin, R. W.; Rhyne, J. J. Spin wave excitations in re-entry para-ferro-spin glass transition in glassy  $(\text{Fe}_x\text{Ni}_{1-x})_{75}\text{P}_{16}\text{B}_6\text{Al}_3$  glasses. Proceedings of the 4th international conference on rapidly quenched metals, 1981. Sendai, Japan. Plenum Press. p. 1153.

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Choi, C. S.; Prask, H. J. Single crystal neutron diffraction study of ammonium nitrate phase III. Acta Crystallogr.; in press.

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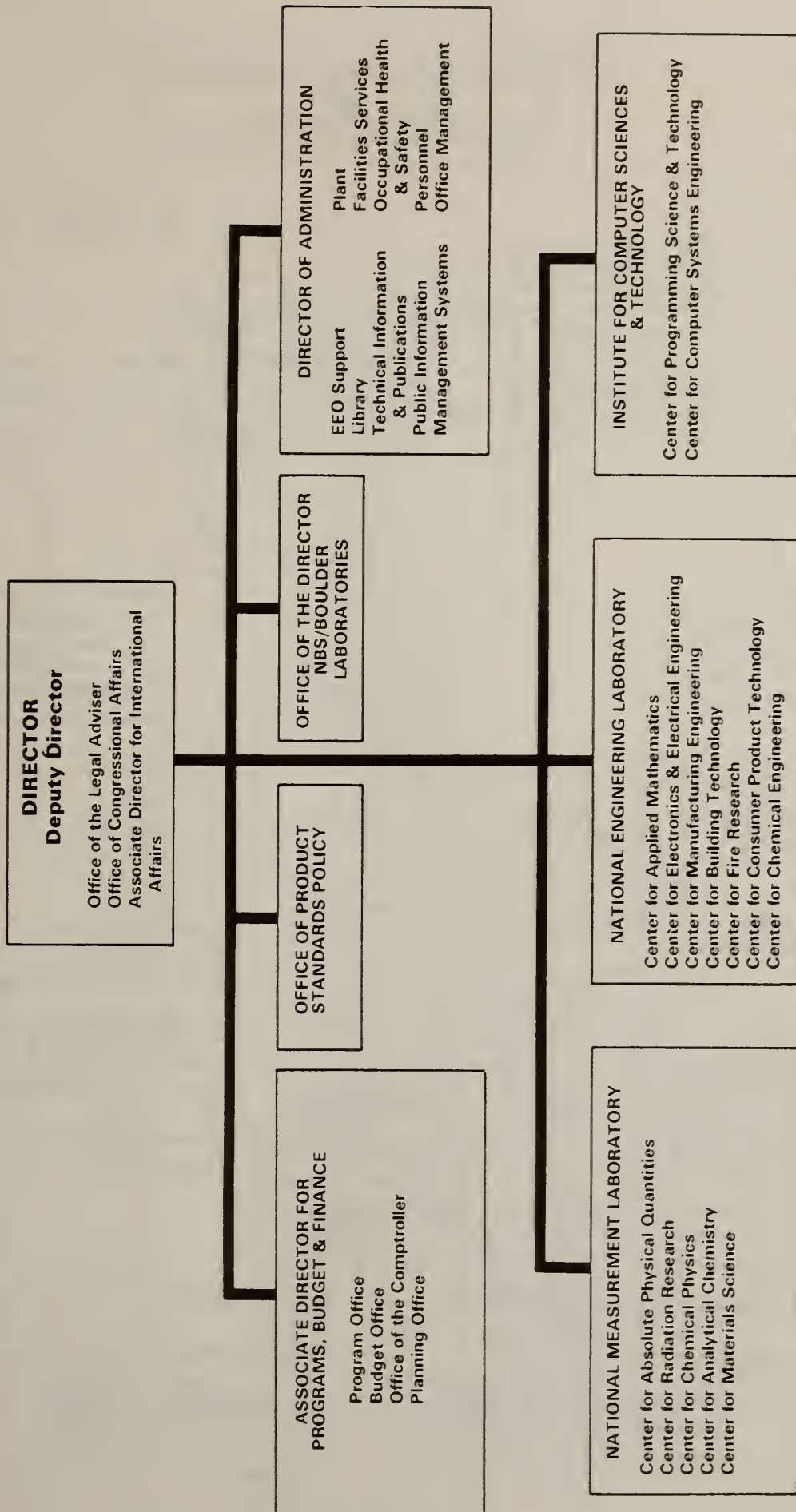
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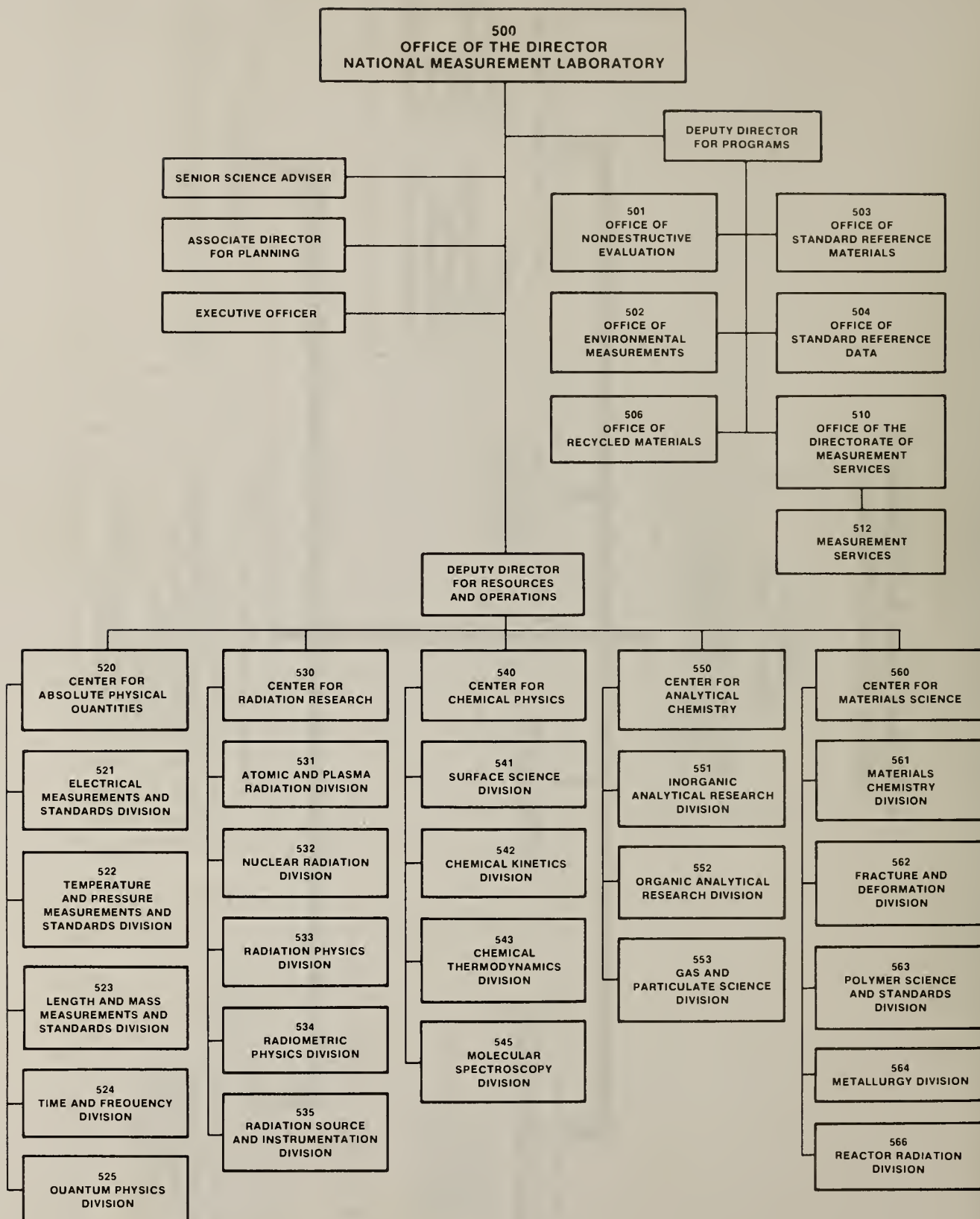
## APPENDIX



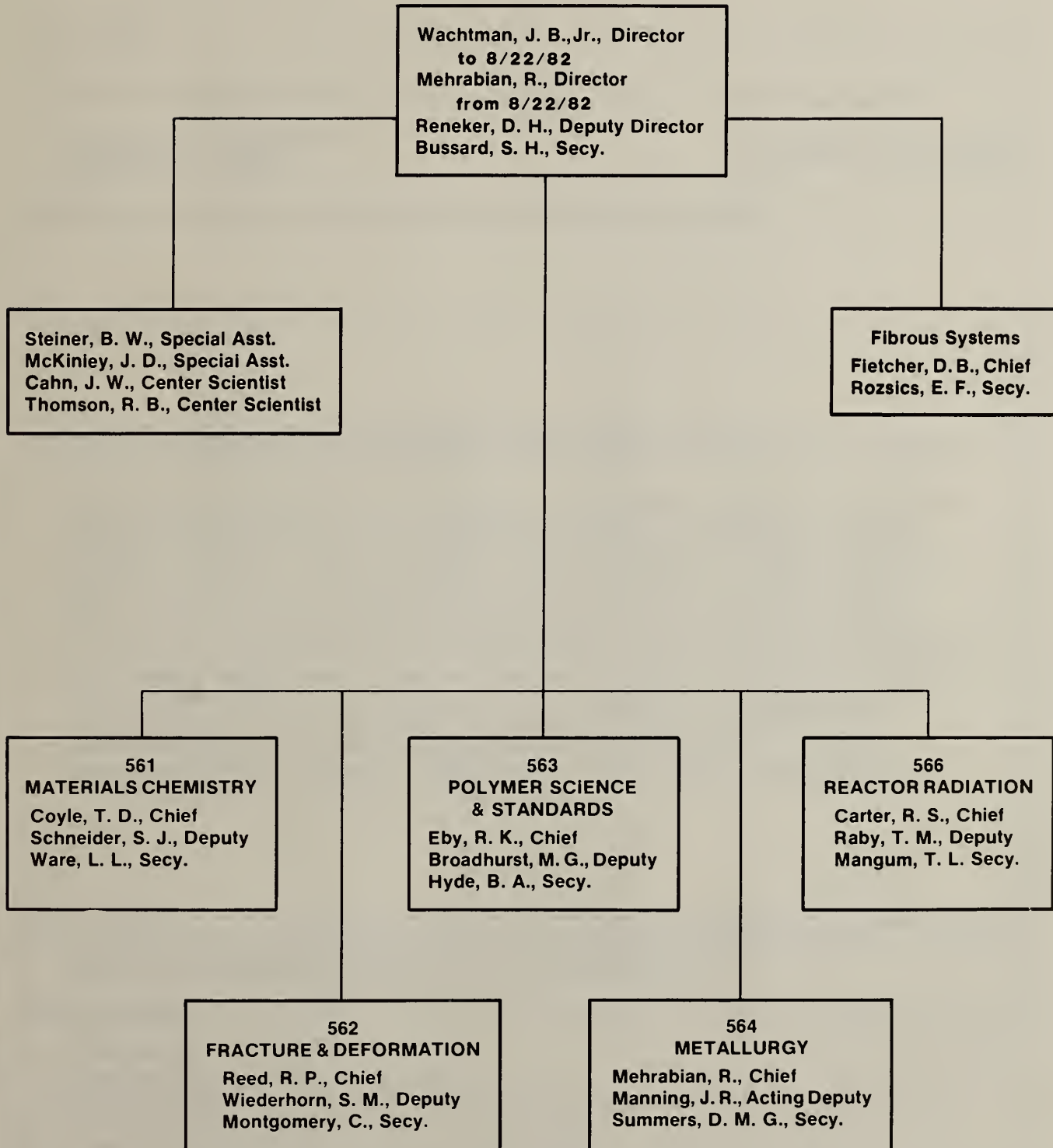


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